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**A MANUAL**  
**FOR**  
**ASSAYERS AND CHEMISTS**

**BY**  
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**FIRST EDITION**  
**FIRST THOUSAND**

**NEW YORK**  
**JOHN WILEY & SONS**  
**LONDON: CHAPMAN & HALL, LIMITED**  
**1910**

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BY

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THE SCIENTIFIC PRESS  
ROBERT DRUMMOND AND COMPANY  
BROOKLYN, N. Y.

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TO THE  
OLD STUDENTS OF THE  
*Missouri and New Mexico School of Mines*  
WHO HAVE INSPIRED ME TO RECORD MY EXPERIENCE  
THIS BOOK  
IS AFFECTIONATELY DEDICATED



## PREFACE

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IN this book I have crystallized my experience of fourteen years as a teacher of chemistry and assaying in technical schools and fifteen years of practical work in the mining districts of the southwest, including Mexico. I write principally for the young graduate of the mining school, thrown upon his own resources for the first time, and brought face to face with conditions and problems unknown to the schools, which he can only solve after years of experience, unless he is given the experience of those who have preceded him. It is presumed that he has learned something of the methods of assaying and has been well trained in chemical manipulation.

I only give those methods which I have used with satisfactory results, giving the actual results of my experience with them; some of the methods are original and, while they have appeared in the journals of the various societies, this is the first time they appear in book form. Some of my methods will be criticised, because they are not in accord with the latest conventional ideas; but technical methods are still in a condition of evolution, and more good can come by faithfully reporting the facts of experience than by trying to avoid hostile criticism by adherence to conventional ideas, whose value is yet to be determined.



An impression prevails that the results reported by technical analysts are less accurate and reliable than those reported by so-called scientific analysts. This is supposed to be due to the superiority of scientific over technical methods, as well as to a lack of skill in technical analysts. The work of all technical analysts is subject to frequent and careful checking by the slowly working scientific chemists, as well as by technical chemists of the highest skill; consequently all technical errors are certain of discovery and the imperfections in the methods are quickly brought to light. It may be that the general impression is correct, but until the work of scientific chemists is subjected to the same rigid checking the data upon which to base an accurate opinion will always be lacking. The results of the scientists ought to be more accurate than those of the technical analysts, because they are not hurried and can take the time to test, step by step, the perfection of each separation; but after everything has been said, the question of method is of less importance than the care and understanding which each individual analyst may put into his work. Technical methods must be quick, and there is a constantly increasing pressure that they shall give results as near to absolute accuracy as is possible to attain. Whatever improvements are desirable in these methods must come from the work of technical analysts, working daily, in absolute touch with the varying conditions in widely separated localities.

The work of Beringer, Furman, and Low in the development of short methods for technical work must always be recognized, and I wish to acknowledge my heavy debt to them and to other writers on the subject. While specific credit is given for each method copied and statement made on the authority of others, there are some

additional items to which I would like to give credit, but I cannot, because I have not available a complete reference library and have forgotten where I secured originally the idea.

I must acknowledge my deep indebtedness to my son, W. H. Seamon, Jr., for his suggestions and help in the experimental work in trying out many new and old methods.

W. H. SEAMON.

CHIHUAHUA, MEX., June 1, 1910.



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# A MANUAL

FOR

## ASSAYERS AND CHEMISTS

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### PART I

#### CHAPTER I

##### ALUMINUM

**1. Ores.** Of all the metallic substances this is the most widely distributed and most abundant in nature. Aluminum, in the form of oxide, is a constituent of all clays and of most rocks. Bauxite is the clay that is mainly employed in the production of metallic aluminum. Cryolite, the fluoride of sodium and aluminum, is also employed in the production of the metal.

**2. Detection.** The substance is treated with hydrochloric and nitric acids, with the aid of heat, in a convenient vessel. After decomposition add sodium peroxide to strong alkaline reaction, filter off the precipitate, preserving the filtrate which contains the aluminum. Make the filtrate acid with hydrochloric acid, add a little ammonium chloride, then ammonia water to alkaline reaction and heat to boiling. A white gelatinous precipitate, permanent on boiling, shows the presence of aluminum.

If the substance is whitish in color and infusible under the blowpipe flame, it may be moistened with a drop of

a solution of cobalt nitrate and reheated, when, if the mass turns bluish in color, aluminum may be reported.

**3. Methods.** The technical determination of aluminum in ores and furnace products has been so seldom called for that very little attention has been given by technical chemists to the development of a quick and accurate method. There have been quite a number of new methods proposed by scientific chemists, which were supposed improvements on the involved and laborious methods found in the standard works on chemical analysis, but none of them has fulfilled its promise when subjected to the varying and trying conditions of actual technical work; consequently, technical chemists, when called upon for an alumina determination, have had recourse, usually, to the indirect method, as described in the various editions of Fresenius.

The following direct and volumetric method has been developed in my laboratory, where it has been thoroughly tried out on a variety of substances, and I feel I can safely recommend it to all chemists as an accurate and safe method.

**4. Decomposition.** A half gram of the pulp, or more if the alumina content is low, is placed in a No. 2 casserole and treated with 10 cc. of hydrochloric acid, followed with a few cc. of nitric acid, and after decomposition evaporated to dryness to make the silica insoluble. The dried mass is then treated with 5 cc. of strong hydrochloric acid, and a little water added, followed with the addition of 5 cc. of sulphuric acid if there is any lead present; then filter and wash with hot water. The aluminum will be in solution in the filtrate, which is treated as in 5.

There are many aluminates which cannot be decomposed by acid treatment. These, if there is no lead or

zinc present, may be fused in a platinum crucible with two grams of sodium peroxide; on cooling, boil the crucible and its contents in a casserole with water, when the aluminum will pass into solution as sodium aluminate. The solution is filtered off when it is ready for titration, 5.

If the determination of aluminum is of sufficient importance to require a fusion, the determination of silica will also have to be made by the fusion method; it is therefore more desirable to make one fusion do for the silica and alumina. This method for fusion will be found fully described in section 272.

The acid solution of the aluminum salts, however obtained, is treated with an excess of sodium peroxide (two grams is usually sufficient) and boiled. A precipitate of iron hydroxide is formed which is filtered off through a 15-cm. filter and washed thoroughly with hot water, saving the filtrate, which contains the aluminum as sodium aluminate, for titration.

The preceding directions are applicable when it is desired to follow them, but it will probably be found advisable in most instances when an alumina determination is required to start with the hydroxide precipitate formed by the addition of ammonia water in preparing the solution for the determination of lime. This precipitate is washed with a boiling solution of ammonium chloride to remove any zinc present. After washing, the precipitate is dissolved, with the aid of heat, in the least quantity of hydrochloric acid, after which sodium peroxide is added in excess and the iron precipitate filtered off and washed.

**5. Titration.** Five cc. of phenolphthalein solution are then added, and ordinary dilute sulphuric acid added until a precipitate begins to form which redissolves on

stirring, being careful not to pass the neutralization point. Then run in standardized sulphuric acid from a burette to point of neutralization. It is unnecessary to measure this addition. Then add a measured quantity of standardized sulphuric acid so there will be an excess, and heat to boiling, when the solution will become clear. A standard solution of potassium hydroxide is then run in from a burette to determine the excess of sulphuric acid, being careful to make a fresh addition of the phenolphthalein solution. The solutions of potassium hydroxide and sulphuric acid having been standardized against each other, the cc. of excess acid are deducted from the measured quantity added, from which the weight of alumina may be calculated.

**6. Standardization.** Special solutions of sulphuric acid and potassium hydroxide should be made for the alumina determination. The standard solution of sulphuric acid is made by adding 8.3 cc. of sulphuric acid, sp.gr. 1.84, to a liter of distilled water, mixing thoroughly and cooling to room temperature before standardizing. Such a solution should give a strength of one cc. equal to 0.005 gram of  $\text{Al}_2\text{O}_3$ . This should be determined by dissolving 1 gram of potassium alum in 100 cc. water, adding 2 grams of sodium peroxide and boiling to drive off the gas evolved. Then add 5 cc. of phenolphthalein solution and run in sulphuric acid until the alkali is just neutralized; then add 20 cc. of the standard solution of sulphuric acid and heat to boiling to make the solution clear. Then add more of the phenolphthalein solution and run in the standard solution of potassium hydroxide to faint alkaline reaction. Deduct the cc. of the standard sulphuric acid solution neutralized by the potassium hydroxide solution, which will give the cc. of sulphuric acid corresponding to the alumina in the alum. As pure alum contains 10.86 per

cent of  $\text{Al}_2\text{O}_3$ , 0.1086 divided by the cc. of sulphuric acid used will give the strength.

A solution made by dissolving 16.4 grams of potassium hydroxide in a liter of water will give a liquid of which one cc. of the alkali will equal one cc. of the acid. This must of course be determined by titrating a measured quantity of the one against the other.

**7. Chemistry.** Sodium peroxide accomplishes a perfect separation of all the other members of the fourth group from alumina and zinc. The alumina enters solution as sodium aluminate  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3$ . This compound has an alkaline reaction and is perfectly soluble in pure water. On adding  $\text{H}_2\text{SO}_4$  to the solution of aluminate, the acid first acts on the excess of soda which is present; next it begins to act upon the sodium aluminate, forming sodium sulphate, which enters solution, and aluminum hydroxide, which forms the characteristic gelatinous precipitate. So long as there remains any sodium aluminate undecomposed, the alkaline reaction persists. When the neutralization point is reached, and the excess of sulphuric acid added and the solution boiled, the aluminum enters solution as the sulphate.

Phosphoric acid if present follows the iron on the addition of the sodium peroxide. Arsenic follows the alumina as sodium arsenate. Lead follows the alumina as sodium plumbate, and the zinc as sodium zincate also follows the alumina. As these compounds would act upon the sulphuric acid, it is much safer to start the alumina determination with the precipitate of iron hydroxide formed on the addition of ammonia water, and washing it thoroughly with a boiling hot solution of ammonium chloride, as indicated under section 4.

It will be observed that there is really nothing very new in this method, and that use has only been made of well-

known facts whose application to the determination of alumina has been overlooked until now. KOH has been used to separate alumina from iron, taking advantage of the solubility of potassium aluminate. The common impurities in KOH have always been an objection to this method. It is now something like fifteen years since an article was published in the *London Chemical News* calling attention to the action of sodium peroxide on the members of the fourth group of metals. But it is only in recent years that chemical manufacturers have furnished sodium peroxide, nearly pure, with a constant amount of alumina as an impurity. For these reasons the use of the peroxide has been delayed. To-day it is quite easy to secure sodium peroxide with no more than one hundredth of one per cent of alumina as an impurity.

By following the directions given the error in the alumina determination should not exceed two hundredths of one per cent.

**8. Gravimetric Method.** Take the solution of sodium aluminate formed by the action of the sodium peroxide after filtering off the iron; make it acid with hydrochloric acid, add half a gram of sodium phosphate, and when it is dissolved add ammonia water in excess and boil the solution for ten minutes." Then filter off the precipitate of aluminum phosphate, wash thoroughly with hot water, and ignite in an annealing cup, starting at a low heat, and weigh as  $\text{AlPO}_4$ . Multiply this weight by 0.4185 to obtain the weight of  $\text{Al}_2\text{O}_3$ .

Be sure to wash out all of the sodium phosphate by the liberal use of hot water, as the gelatinous precipitate tends to retain the sodium salts mechanically.

**9. Uses and Valuation.** On account of the lightness of the metal it is employed in a small way for many diverse applications. It is a good conductor of electricity and is

now being used for this purpose in carrying large currents from Niagara Falls to Syracuse, a distance of 160 miles, and also to Cleveland, a distance of 200 miles. At the present time metallic aluminum can be bought in New York at twenty-three cents per pound, and in Germany for fourteen cents per pound. It is stated that the metal is now being produced in France at a cost of nine cents. It is therefore probable that aluminum will soon have a higher place among the commonly used metals than it has heretofore held.

Bauxite furnishes the chief supply for the metal, and it sells for \$4.50 per ton f.o.b. at the mines. Cryolite is used to assist in the extraction, and it sells at \$14 per ton in New York.



## CHAPTER II

### ANTIMONY

**10. Ores.** Antimony occurs as stibnite (the sulphide), and senarmontite (the oxide), these two minerals constituting the only true ores of the metal. There are, however, many other complex sulphides and oxides in which antimony occurs associated with copper, lead, silver, gold and zinc. While most of the pure antimony employed in commerce is obtained from stibnite, there is a large percentage derived from the refining of the base bullion obtained in the smelting of lead ores.

**11. Detection.** Mix a small portion of the substance, well powdered, with dry sodium carbonate and heat it with the reducing flame of the blowpipe, on charcoal. Antimony is volatilized and partially condensed as a white coating; moisten it with a drop of a solution of ammonium sulphide, when the formation of the orange red color of antimony sulphide will unerringly determine its presence, even when the amount is small.

**12. Desiderata.** In smelter practice the shipper of ore wishes a low result, as antimony is detrimental, and is fined at the rate of from twenty-five to fifty cents per unit for all over three per cent. In some localities the fine is assessed at the same rate for the antimony arsenic and bismuth when their percentages combined is one per cent and over. By careful work on the part of the assayer the determination of antimony by any of the following methods will be correct. It is not possible to secure a result higher than the actual content of the pulp.

By slurring the work a lower result can be secured, and as the ore shipper does not like to pay the penalty for antimony his assayer does not receive any credit for careful work.

**13. Decomposition.** The pulps should be finely divided, passing a 200-mesh sieve. A mixture of equal parts of dry sodium carbonate and sublimed sulphur is previously made, of which five grams are weighed out and placed in a No. 2 porcelain crucible. A half gram of the pulp is mixed with this, and the whole covered with about three grams of the fine mixture. A cover is then placed on the crucible, which is then heated in a gas, or Dangler lamp, flame until the fumes of sulphur cease to come off. A high heat is necessary. After cooling, the crucible is placed in a No. 3 casserole, covered with water, and warmed until the fused mass is disintegrated. A stirring rod may have to be employed to make a perfect solution. Then remove the crucible and cover, and rinse off with water. A yellowish colored solution of antimony (possibly with arsenical or stannous) sulpho salts will be obtained with a black residue of iron sulphide, mixed with copper, lead and other sulphides whose metals may be present in the ore. The solution is filtered off, the filtrate being caught in a 300-cc. beaker, and the residue washed with a solution of sodium, or potassium, sulphide.

The filtrate is acidulated with acetic acid of twenty-five per cent strength, resulting in the formation of a precipitate of sulphur mixed with the antimony sulphide, also with the sulphides of arsenic and tin if they are present. Allow the precipitates to settle before filtering and keep as much as possible of it in the beaker, washing with hydrogen-sulphide water. The arsenic may be removed by treating the residue in the beaker and on the filter with a warm solution of ammonium carbonate.

Unless the percentage of arsenic is very large, three washings with the ammonium carbonate will remove all of it. Tin is an uncommon constituent of compounds in which antimony determinations are called for. If it is present it must be removed by special methods, and I know of no method more reliable than that of Mr. Low.\*

**14. Gravimetric Determination.** The antimony sulphide is then treated with a warm solution of ammonium sulphide, which dissolves the antimony, and the solution is caught in a casserole and evaporated to dryness, completing the evaporation on a water bath, or at a very low heat. Moisten the residue with a little strong nitric acid and oxidize as completely as possible all of the sulphur, as well as the antimony. Then boil down to small bulk and transfer to a porcelain crucible, and complete the evaporation until all of the sulphuric acid is driven off. Then ignite the crucible and its contents at a bright red heat. The crucible is then weighed and the weight of  $\text{Sb}_2\text{O}_4$  determined. This weight multiplied by 0.7895 will give the weight of the antimony.

Any arsenic left in the residue will be volatilized by the high heat, while all tin will remain as the stannic oxide, increasing the apparent amount of antimony.

**15. Volumetric Method.** The precipitate of antimony sulphide, after removal of the arsenic, is transferred to a beaker, covered with 15 cc. of a concentrated solution of mercuric chloride, and the whole is boiled hard until all the orange red colored precipitate of antimony sulphide is gone and only a white, or yellowish, residue remains. If much antimony be present and more mercuric chloride is required, it is best to add the additional

\*Journal of the American Chemical Society, page 1715, Vol. XXVIII.

amount by using the crystals of mercuric chloride. The boiling must be continued until all sulphur dioxide is volatilized; the solution is then filtered and the residue washed with dilute hydrochloric acid. In this manner a solution of antimonous chloride is secured. Water is added until the solution becomes turbid, and then just enough dilute hydrochloric acid is added to clarify the liquid; afterwards one gram of Rochelle salt is added. If only small amounts of antimony are present, the turbidity made by the addition of water may not be noticeable. If no turbidity is shown after the addition of 150 cc. of water, it is then only necessary to add 25 cc. of dilute hydrochloric acid, when the solution will be ready for titration as soon as it has cooled to room temperature.

**16. Titration.** The solution is titrated with a potassium permanganate solution until the first permanent pink is obtained. The solution commonly used for iron may be employed, and the factor for antimony determined from that for iron, multiplying the latter by 1.0751; or it may be determined directly by weighing out a portion of antimonous oxide, or tartar emetic, and dissolving it in dilute hydrochloric acid. The method gives reliable results and is capable of great accuracy. The danger points to be particularly watched are the decomposition of the ore and the proper amount of hydrochloric acid at the time of titration.

**17. Precipitation of Sulphide.** The alkaline sulpho solutions of antimony are completely precipitated by dilute acetic acid. By warming the solutions, and using one to four acetic acid, the density of the precipitate is increased and the liquid clears most rapidly, and the separation of free sulphur is reduced to a minimum. Filtration, when once begun, should be steadily pushed until completion of the operation and washing with

hydrogen sulphide water. If the precipitate is left uncovered it is liable to oxidize partially, and some antimony will pass through.

**18. Removal of Arsenic.** The employment of a warm saturated solution of ammonium carbonate to dissolve the arsenous sulphide associated with antimony sulphide I have found quite satisfactory. It is needful to wash out the sulpho salts carefully before treating with the ammonium carbonate solution, or else there is the possibility of the formation of some ammonium sulphide and a partial solution of the antimony. Three washings have removed all of the arsenic when there was three times as much arsenic present as there was of antimony.

**19. Re-solution of the Sulphide.** Boiling with concentrated hydrochloric acid in the presence of mercuric chloride results in the complete solution of the antimony and the formation of sulphides of mercury.

**20. Titration.** The presence of tartaric acid does not interfere with the permanganate titration when the amount of acid is not greater than three times that of the antimony. Varying quantities of the hydrochloric acid give widely varying results, irregular in character. Fresenius states that there should be one-sixth of the volume of liquid of hydrochloric acid of 1.12 sp.gr., and I have found it essential to follow closely the directions given. I have also found that varying the amount of antimony with a constant amount of hydrochloric acid showed the advisability, when accuracy was highly essential, of employing factors corresponding approximately to the amount of antimony present.

Titration should be made as soon as the solution is of proper temperature, as there is a tendency for the deposition of antimony basic salts on standing which cannot be taken up again by the addition of hydro-

chloric acid. Rochelle salt is used to diminish this precipitation.

**21. Nissenson and Seidler Method.** The ore is brought into solution, using twenty cc. of concentrated hydrochloric acid for half a gram of the ore, or more if the antimony is low in amount. Bromine is added to the hydrochloric acid, and the operation is conducted in a flask, which is shaken from time to time and kept in a warm place. The solution is strongly boiled to drive off all the bromine, and after it has cooled, sufficient sodium sulphite crystals are added to reduce the solution. It is then boiled to drive off all the sulphur dioxide. Twenty cc. of hydrochloric acid are then added and the liquid heated to the boiling point. It is then titrated hot with a standard solution of potassium bromate.

Three drops of an indigo solution are added as an indicator, and the titration is conducted to a very faint green coloration. It is well to add a little fresh indicator just previous to the end-point.

The indicator solution is made by dissolving powdered indigo in fuming sulphuric acid. The powdered indigo is added slowly to the acid in the ratio of one part of the indigo to five parts of the acid. It should be kept as cool as possible while making the solution, and ought to be allowed to stand for twenty-four hours before using.

The standard solution of potassium bromate is made by dissolving 2.7852 grams of the salt in a liter of water. It is standardized by dissolving half a gram of tartar emetic in thirty cc. of concentrated hydrochloric acid, heating to boiling, reducing with sodium sulphite as previously described, and titrating hot. The crystallized c.p. tartar emetic contains 36.16 per cent of antimony.

When the ores cannot be decomposed with hydrochloric

acid, it is necessary to decompose them by the fusion method (see section 13).

The alkaline solution thus obtained is acidulated with acetic acid, and the antimony sulphide filtered off and washed, after which it is easily dissolved in thirty cc. of concentrated hydrochloric acid, after which the treatment is as before described.

**22. Uses.** Antimony is chiefly used in the form of alloys, especially type and babbitt metals. The sulphide is much employed in vulcanizing processes for rubber, Antimony pigments are more permanent than zinc, and less injurious to health than the lead pigments, and it may be that quite a demand may be worked up in this line.

**23. Valuation of Ores.** The selling price of antimony ores is based upon the selling price of metallic antimony, or regulus, in the London market. When this sells at \$170.00 per ton of 2240 lbs., ore carrying fifty per cent of metallic antimony is worth \$50.00 per long ton or \$40.00 per short ton f.o.b. London. For each unit over fifty per cent a premium of \$1.00 per long ton was paid and for each variation in price of regulus of \$2.50 per long ton a corresponding reduction, or addition, of 62½ cents per long ton is made. Ores running less than forty per cent are usually not accepted by the smelteries, they being too low grade for smelting economically.

## CHAPTER III

### ARSENIC

**24. Ores.** The only mineral that may be considered an ore of arsenic is arsenopyrite. There are many minerals containing small amounts of arsenic which occur associated with the lead, silver and copper ores.

**25. Detection.** Mix a small portion of the finely divided substance with three parts of dry sodium carbonate and powdered charcoal, place it in the bottom of a closed tube, and heat gently; a steel gray sublimate of metallic arsenic will be found.

**26. Methods.** On account of its wide distribution and association with the silver-lead ores its determination is a matter of considerable importance, as heavy fines are laid upon arsenic by the silver-lead smelters. The Pearce method is the one generally employed, and the one used in my laboratory is Low's modification of Pearce's method.

**27. Decomposition, Dry Method.** A mixture of equal parts of dry sodium carbonate and potassium nitrate is kept on hand for immediate use; half a gram of the finely divided pulp is thoroughly mixed with three grams of the fusion mixture and placed in a porcelain crucible or a platinum dish; the mass is covered with another three grams of the fusion mixture and the whole is heated gradually in the flame from a Dangler lamp, by which the mass can first be most strongly heated at the top. Heating in this way the fusion mixture is more certain to envelop the particles of pulp, ensuring most perfect oxidation and



fusion, reducing loss of arsenic by volatilization to a minimum. The heat is then increased and prolonged until the fusion is complete and perfectly liquid. This requires only a few minutes, except in certain oxidized ores of lead. If the ore is a heavy sulphide, it must first be treated with nitric acid and evaporated to dryness, and then fused with the fusion mixture.

**28. Ebaugh and Sprague's Method for Decomposition.\***

One part of dry sodium carbonate and four parts of zinc oxide are mixed thoroughly. One-half a gram of the pulp is mixed intimately with 5 to 10 grams of the fusion mixture of zinc oxide and sodium carbonate and placed in a porcelain crucible of about 50 cc. capacity; a layer of the reagent mixture is next added, and the whole heated to redness in a muffle for from 15 to 20 minutes. After removal from the muffle it is cooled and the melt extracted with water. The alkaline filtrate is acidified with acetic acid and the arsenic precipitated with silver nitrate, as in section 31.

The advantages claimed for this method of decomposition are: (1) The mass resulting from the heating is not fused but can be rapidly removed from the dish and leached with water; (2) the ease and speed with which sulphides, sulphates, arsenates, etc., are decomposed; (3) no time consuming evaporations are necessary; (4) the absence of a large quantity of alkaline and other salts from the solutions in which the precipitates are effected.

I have tried this method for several varieties of pulps and find the advantages to be as stated in the trials I made. The same method is recommended as an improvement on Eschka's method for sulphur determinations.

\* Western Chemist and Metallurgist, Vol. III, p. 149.

**29. Wet Method.** When the arsenic is in the form of impure white arsenic it is most readily obtained in solution by boiling with a solution of sodium hydroxide. If in the form of mineral, or ores, half a gram of it is treated in a casserole with ten cc. of strong nitric acid to oxidize the arsenous acid to arsenic acid, warming it; and if necessary to evaporate to dryness the evaporation must be made on a water bath. Sodium peroxide is added in excess to the acid solution and hydrogen sulphide gas is passed through the warm solution in excess, then filter, and wash the precipitate with water containing sodium sulphide. The filtrate will contain the arsenic, together with any antimony and tin that may have been in the pulp. The filtrate is acidulated with acetic acid and thoroughly saturated with hydrogen sulphide gas, and the precipitated sulphides filtered off and washed with hydrogen sulphide water. The washed sulphides are then removed from the filter and boiled with ten cc. of concentrated nitric acid in a beaker, and the solution diluted and filtered to remove any globules of sulphur. Sodium peroxide, free from phosphoric acid or sodium carbonate, is then added in excess, when the solution will contain all of the arsenic, free from phosphoric acid, as sodium arsenate. The solution may be titrated with uranium acetate, or treated by the Pearce method, as described in section 31. When the pulp contains phosphoric acid the wet method of decomposition should be always followed.

**30. Solution.** The melt obtained by fusion is boiled with water in a large casserole until the mass is completely disintegrated; a glass rod may be used to facilitate the breaking up. After being completely disintegrated, the solution is filtered and the filtrate collected in a flask of sufficient size.

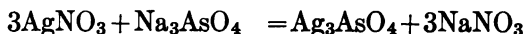
**31. Precipitation as Silver Arsenate.** The solution obtained by digesting the fused mass in the dry fusion method is placed in a flask, and a piece of litmus paper is placed in the solution and acetic acid cautiously added to feeble acid reaction. Twenty cc. of a solution of 34 grams of silver nitrate in a liter of distilled water are then added. This amount will be sufficient provided there is not more than fifteen per cent of arsenic in the pulp. On the addition of the silver nitrate a white precipitate will form. Ammonia is then cautiously added to dissolve this precipitate of the chloride, leaving the red silver arsenate undissolved. Then make the solution feebly acid with acetic acid, add three grams of sodium acetate, and boil; all of the arsenic will be precipitated together with more or less silver chloride; allow to cool to room temperature, then filter, when the filtrate should be clear. Wash the filter with cold water until all silver salts are washed out. Then remove the beaker and place a clean beaker under the funnel, and dissolve the silver arsenate with cold dilute nitric acid, and wash with cold water. The solution is then ready for titration with ammonium sulphocyanate.

**32. Titration with Ammonium Sulphocyanate.** Five cc. of a strong solution of ammonio-ferric alum is added to the solution and a standard solution of ammonium sulphocyanate is run in until the liquid becomes permanently red, being careful to shake the vessel frequently so as to break up all clots. The end reaction is sharp and cannot be mistaken.

**33. Standardizing Ammonium Sulphocyanate.** The standard solution is made by dissolving 7.617 grams of ammonium sulphocyanate in a liter of distilled water. Its strength is determined by dissolving 0.2 gram of pure silver in a little nitric acid; dilute to 100 cc. and add 5 cc. of a strong solution of ammonio-ferric alum and run the

sulphocyanate solution, from a burette, until a permanent red tint is produced. The weight of silver divided by the number of cc. used gives the strength of the solution in silver per cc.; this weight multiplied by 0.2317 gives the arsenic value, which should be about 0.0025 gram of arsenic per cc. The solution of sulphocyanate should be kept in a dark bottle, away from strong light and the air. It keeps very well, but should be restandardized once every two weeks.

**34. Chemistry of Pearce Method.** The arsenic is in solution as sodium arsenate probably a mixture of  $\text{NaH}_2\text{AsO}_4$  and  $\text{Na}_3\text{AsO}_4$ . On the addition of the silver nitrate the following reactions may occur.



Sodium acetate is added to prevent the formation of much free nitric acid, forming sodium nitrate and free acetic acid. If much arsenic is present there may be formed too much free acid, in which event the addition of a little ammonia may be necessary to complete the precipitation. The critical period of the method is found at the precipitation with silver nitrate, and the analyst must be sure of himself at this stage.

On the addition of sulphocyanate to the solution the silver is precipitated as  $\text{AgSCN}$ . The titration is not affected by variations in temperature between  $15^\circ$  and  $60^\circ$  C.; by variations in the amounts of nitric acid from one to fifteen cc.; or by variations in the amounts of sodium and ammonium salts. The disturbing factors are the presence of molybdic and phosphoric acids. These acids

are precipitated by silver nitrate, and consequently would increase the amount of arsenic; with uranium acetate the error from molybdic acid is removed; but the error from phosphoric acid can only be obviated by precipitation of the arsenic as the sulphide, as described in the wet method for decomposition in 29.

Loss of arsenic by volatilization in the fusion method, if proper care is taken, is small. The results by dry method are therefore very likely to be lower than the real arsenic content. The results by the wet method of decomposition are usually higher than by the dry fusion method, but it must be borne in mind that solutions of arsenic containing hydrochloric acid cannot be evaporated without loss of arsenic as the chloride.

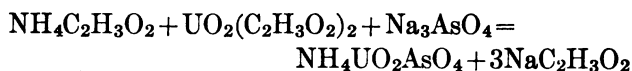
I prefer the decompositions by the fusion method, and only use the wet method occasionally, when there seems to be good reason to do so.

**35. Titration with Uranium Acetate.** The arsenic is obtained in solution as arsenate by the dry or wet methods of decomposition. The solution is first made feebly acid with nitric acid, then feebly alkaline with ammonia water, when three grams of sodium acetate are added and enough acetic acid to make the solution feebly acid. Dilute to 150 cc., heat to boiling, and run in a standard solution of uranium acetate from a burette until a brown coloration is made on the spot plate with a potassium ferrocyanide indicator. It is well to reserve a portion of the solution, and after quickly reaching an end reaction add it and work more slowly to secure the end reaction.

**36. Standardizing Uranium Acetate.** The indicator solution is made by dissolving 10 grams of potassium ferrocyanide in 100 cc. of distilled water. The standard solution of uranium acetate is made by dissolving 34 grams of the salt in 500 cc. of distilled water and 25 cc. of acetic

acid, and diluting to a liter. To standardize, weigh out 0.2 gram of  $\text{As}_2\text{O}_3$  into a beaker and boil with a sodium or potassium hydroxide solution until it is dissolved; make acid with nitric acid, boil for a few minutes, and dilute to 150 cc. after first making alkaline with ammonia water; add 3 grams of sodium acetate and make acid with acetic acid. The solution is titrated hot, and the final temperature should not be below  $33^\circ\text{C}$ . The weight of  $\text{As}_2\text{O}_3$ , multiplied by 0.757, and this weight divided by the cc. consumed, will give the strength of each cc. in As.

**37. Chemistry of Uranium Acetate Method.** When the solution of uranium acetate is run into solution of the arsenate, arsenic is precipitated as a yellow precipitate.



A solution of arsenic was made of such strength that 25 cc. required 20 cc. of the standard solution, and the following variations were examined:

**38. Varying Temperatures.**

Temperature of titration.....	15°	20°	40°	80°
Uranium acetate used (cc.) ..	18.9	19.2	20	20.1

The reaction with the indicator is more active in the cold than when hot, and the titration should be completed before the temperature falls below  $40^\circ\text{C}$ .

**39. Varying Bulk.** The titration was begun at the boiling temperature and concluded before it fell to  $40^\circ\text{C}$ .

Bulk (cc.).....	50	100	150	200
Uranium acetate used (cc.) ..	19.80	19.8	20	20.1

**40. Varying Sodium Acetate.** The bulk was 150 cc. at commencement of titration and the temperature as before

Sodium acetate (grams) ....	1	2	4	8	16
Uranium acetate used (cc.)..	20	20	20	21.5	24

No more than five grams of sodium acetate should be used, and the same results were found when ammonium acetate was employed. It is likewise found inadvisable to employ an excess of acetic acid over and above four cc.

Iron and aluminum salts must be absent, and in the event there are no phosphates present I find the method very satisfactory.

**41. Valuation.** It cannot be said that there is any regular market for arsenic ores. The world's supply of arsenic is almost entirely secured from the flue dust of the various smelting works where arsenical ores are treated, and this supply has been sufficient, so far, for the demand. Pure white arsenic is worth from three to four cents a pound in quantity, and the demand for it comes from the calico printers, the manufacturers of shot, and the preparation of the insecticides, and in the tanning industry.

**42. Remarks.** Arsenic is detrimental in the smelting of silver and gold ores, and the smelters fine the ore shippers for it on the same basis as for antimony.

## CHAPTER IV

### BARIUM

**43. Ores.** Heavy spar (the sulphate), and witherite (the carbonate), are the most commonly occurring minerals of barium.

**44. Detection.** The salts of barium color the flame green and this test is sufficiently characteristic to the experienced eye. The green is different in color from the green of copper and boric acid.

**45. Methods.** Barium is usually determined by the gravimetric method, weighing it as barium sulphate. The volumetric method described in this chapter will be found satisfactory, and when many barium determinations are required daily its use is recommended. If there are no sulphates in the pulp, the barium can be readily dissolved by the conventional acid treatment. But barium sulphate is the most commonly occurring mineral of barium, and it is therefore best to start a barium determination by the fusion method of decomposition.

**46. Decomposition.** One half gram of ore is treated with hydrochloric and nitric acids, as described in section 270.

When decomposition is complete add five cc. of concentrated sulphuric acid, which precipitates all the barium as the sulphate. Five grams of ammonium chloride are added, and the insoluble residue is filtered off while the solution is boiling hot. The ammonium chloride is to dissolve any lead sulphate present, and in the absence of that metal the addition of the chloride may be omitted.



The precipitate and filter are ignited in a platinum crucible, and after cooling, the residue is mixed with three grams of potassium carbonate and an equal amount of sodium carbonate and the whole brought to perfect fusion. The crucible and its contents are then cooled, and boiled in a casserole with water for the purpose of disintegrating the mass and dissolving all of the alkaline sulphates; these must be completely washed out and the insoluble barium carbonate filtered off. The subsequent treatment depends upon whether the determination is completed by a volumetric method or by the gravimetric.

**47. Gravimetric Method.** The barium carbonate is dissolved with five cc. of strong hydrochloric acid and the solution, with the washings from the filter paper, collected in a beaker of about 200-cc. capacity. The solution should have a volume of about 100 cc. It is heated to the boiling temperature and dilute sulphuric acid added slowly, so as to keep the liquid boiling all the time, until there is an excess; about thirty cc. of the ordinary dilute sulphuric acid is sufficient for the largest amount of barium. The sulphuric acid is added slowly to avoid loss from the rapid evolution of hydrochloric acid, and also to make the barium sulphate more dense, causing it to filter with the least difficulty. The solution is then allowed to settle in a hot place. It is then filtered through a closely woven filter, washed thoroughly with warm water, and the filter and contents ignited in an annealing cup in the muffle and the whole weighed, by dusting it into the scale pan, as barium sulphate.

In smelter work the total barium in the ore is regarded as existing as sulphate, and barium is always so reported. To obtain the weight of  $\text{BaO}$  multiply the weight of  $\text{BaSO}_4$  by the factor 0.6571.

**48. Short Method.** The following short method will give results that can be depended upon, provided care is taken to drive off all the silicic acid. After the preliminary acid treatment, instead of igniting the barium sulphate and insoluble residue in a platinum crucible, use a platinum dish for the ignition; after cooling, add two cc. of hydrochloric acid and five cc. of hydrofluoric acid and evaporate at gentle heat to dryness; repeat this operation, and after going to dryness the second time weigh the dish and contents; then repeat the treatment with hydrochloric and hydrofluoric acids and weigh again; if there has been no loss in weight it is quite certain that all of the silica has been driven off; there may yet remain alumina and other elements that were combined with the silica, and the determination can be made more accurately by treating the residue again with hydrochloric acid, and diluting with hot water; filter, wash well with hot water, and ignite the filter and contents in an annealing cup and weigh as  $\text{BaSO}_4$ . Multiply by 0.6571 to obtain weight of  $\text{BaO}$ .

**49. Volumetric Method.** The following method is quick, and more accurate than the gravimetric, as described above. Starting with the barium carbonate on the filter, it is all washed with a strong jet of water into a beaker, unfolding the filter to insure the removal of all the barium carbonate. One hundred cc. of standardized sulphuric acid is added and the whole solution heated to boiling. The sulphuric acid decomposes the carbonate, forming barium sulphate; the carbonic acid boiling away, a drop of phenolphthalein is added to the partially cooled solution and the excess of sulphuric acid determined by titrating with a standard solution of potassium hydroxide, of which one cc. equals one cc. of the sulphuric acid. Use a sulphuric acid solution made by dissolving 1.2 cc. of sulphuric acid,

1.84 sp.gr., in a liter of water. One cc. of a solution of this strength will equal approximately 0.005 gram of  $\text{BaSO}_4$ . It is standardized by weighing out 0.1 gram of precipitated barium carbonate into a beaker, adding 60 cc. of the standard solution of sulphuric acid and determining the excess of acid, as above, by titrating with the standard solution of potassium hydroxide, of which 1 cc. should equal 1 cc. of the standard acid. By dissolving 2.6 grams of caustic potassa in a liter of water a solution will be had which will be of near the requisite strength. The weight of barium carbonate multiplied by 1.182 and divided by the number of cc. of sulphuric acid consumed will give the value of 1 cc. in grams of  $\text{BaSO}_4$ .

**50. Uses and Valuation.** There is a strong demand for barytes and witherite in the paint trade. For these purposes the minerals should be quite white and free from iron. In certain sections quite an industry has been developed in mining barytes for the paint factories. The clean mineral sells for from \$4.00 to \$6.00 a ton f.o.b. cars at mines. The finished barytes, ground and treated with acids, run from \$14.00 to \$17.00 a ton f.o.b. New York.

**51. Remarks.** In silver-gold smelters no direct penalty is imposed for barytes in the ores; part, and sometimes all, of the barytes present is counted as insoluble and then the sulphur in the barytes pays the common sulphur fine. A wise ore shipper will always ask for a fused silica if his ores carry barytes.

## CHAPTER V

### BISMUTH

**52. Ores.** Metallic bismuth furnishes the greatest portion of the metal. Bismuth ocher,  $\text{Bi}_2\text{O}_3$ , usually mixed more or less with iron, copper, arsenic and lead compounds, is also a source of supply. Bismuth glance,  $\text{Bi}_2\text{S}_3$ , is the only other bismuth mineral that may be considered an ore.

**53. Detection.** A mixture of equal parts of cuprous iodide and sulphur is prepared. One part of the substance to be tested is intimately mixed with two parts of reagent and heated with the blowpipe on a piece of charcoal, with a piece of sheet aluminum placed close to the assay. The aluminum should be hot to prevent condensation of free iodine on its surface. With these precautions the presence of even small amounts of bismuth is made known by a brownish-red deposit of bismuth iodide.

**54. Methods.** Bismuth is usually determined gravimetrically, and the chief difficulty in its determination arises from the tendency of its salts to form basic salts which precipitate on addition of water. This tendency interferes with the accuracy of the various volumetric methods that have been proposed. The smelters buying copper and lead ores penalize the bismuth content on the same basis as for arsenic and antimony, **11**.

**55. Decomposition.** One half to two grams of well powdered ore may be taken and treated in a No. 2 casserole with hydrochloric and nitric acids to decompose it. After

decomposition the solution is boiled down to soft dryness and five cc. of sulphuric acid added and the solution boiled until strong fumes of sulphuric oxide are evolved, to convert all lead and barium salts into sulphates; cool, add water and filter, washing with dilute sulphuric acid. The filtrate will contain the bismuth as bismuthic sulphate. Owing to the tendency of solutions of bismuth salts to form basic salts the solution should be handled promptly.

**56. Precipitation.** The sulphuric acid solution is boiled with a piece of sheet aluminum, which will precipitate all of the bismuth, together with cadmium, copper, mercury, etc., that may be present.

The liquor is decanted off, and after washing once with tap water the metallic precipitate is washed off the aluminum with a water jet and the aluminum thrown aside. The beaker is shaken to unite the metallic residue, and this is washed twice by decantation.

The moist residue is then treated with a mixture of 5 cc. of nitric acid and 5 cc. of water; dilute to 100 cc., partly neutralize with ammonia water, then add a solution of ammonium carbonate in excess and boil; filter and wash with hot water. Dry the precipitate and transfer it from the filter to a small weighed porcelain crucible. Ignite the whole carefully, to avoid fusion, at a low red heat; cool and weigh the  $\text{Bi}_2\text{O}_3$ . Multiply this weight by 0.8968 to secure the weight of metallic bismuth.

**57. Uses.** The metal is used in the manufacture of fusible alloys, for dentists' use, and stereotyping; certain of its salts are employed medicinally. About five hundred tons annually is sufficient to supply the present needs of the world.

**58. Valuation.** The price of the metal varies between 73 cents and \$2.50 per lb. In ores where the percentage

of bismuth is small, 10 cents per lb. has been paid for each pound of bismuth carried by the ore. Ores carrying 30 per cent and more have been sold at the rate of \$1.00 per lb. of bismuth when the pure metal was sold for \$2.25 per lb.

## CHAPTER VI

### CADMIUM

**59. Ores.** There is but one mineral occurring in nature with a high percentage of cadmium, and that is greenockite; but it is not, however, found abundantly enough to constitute an ore. Cadmium occurs with zinc in several zinc minerals, and it is as a by-product in the smelting of zinc that the cadmium of commerce is secured.

**60. Detection.** Boil the substance suspected to contain cadmium with sulphuric acid. Then boil with aluminum foil. Dissolve the precipitated metals in a little nitric acid, make alkaline with ammonia and decant if there is a precipitate. Acidulate with hydrochloric acid and add potassium ferrocyanide. If cadmium is present a white precipitate will result. If copper is present the red copper ferrocyanide may obscure the cadmium ferrocyanide. In this event dissolve the precipitate in potassium cyanide, make alkaline with ammonia, and add ammonium sulphide. Cadmium gives a yellow precipitate.

**61. Decomposition.** Take half a gram of the ore in a No. 2 casserole and treat with 7 cc. nitric acid and 5 cc. hydrochloric acid, heating until the ore is decomposed; evaporate to soft dryness, add 5 cc. sulphuric acid, and boil until fumes of sulphuric acid come off copiously; filter off and boil with metallic tin, when copper, bismuth, mercury, arsenic and antimony that may be present will be thrown down. The tin and metallic residue is separated by removal of the tin and filtration. This filtrate

is then boiled with metallic aluminum, which precipitates the cadmium.

**62. Treatment of Metallic Precipitate.** After the aluminum has precipitated the metallic contents of the solution, water is added, the aluminum is removed and placed on a watch glass; and after the metallic precipitate is settled, the overlying liquor is decanted off and the precipitate washed twice with distilled water by decantation. Seven cc. of nitric acid is then measured off, and the metallic residue in the beaker, and any adhering to the aluminum, is dissolved with it and the two solutions mixed. The nitric acid solution is made slightly alkaline with ammonia and five cc. of concentrated hydrochloric acid are then added, and five grams of ammonium chloride, after which it is ready to be titrated with a standard solution of potassium ferrocyanide.

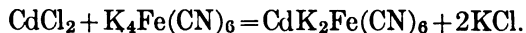
**63. Titration.** The solution of cadmium with a slight excess of hydrochloric acid (less than five cc.), with a bulk of from 150 to 200 cc., is heated to boiling, and a standardized solution of potassium ferrocyanide is run in from the burette in the same way as in titrating a zinc solution until the well-known end reaction, with uranium acetate, or nitrate, as an indicator.

**64. Standardizing.** The same solution of potassium ferrocyanide used for zinc may be used, and the cadmium factor calculated by multiplying the zinc factor by 0.861, but it may be standardized for cadmium by dissolving a weighed amount of pure metallic cadmium in ten cc. hydrochloric acid to which a few drops of nitric acid have been added; when the solution is complete, dilute with water, neutralize with ammonia and acidify with hydrochloric acid, add five grams of ammonium chloride, heat to boiling and then titrate. The weight of cadmium taken divided by the cc. of ferrocyanide used gives the



factor for cadmium. 18.9 grams of potassium ferrocyanide to the liter will give a solution of which one cc. will equal 0.005 gram of cadmium.

**64a. Chemistry.** The reaction is as follows:



**65. Determination of Lead and Cadmium in Spelter.\***

Solution of the sample is here effected by dilute hydrochloric acid, according to Oswald Gunther, or by dilute sulphuric acid (Nissenson) until nearly all zinc is dissolved. The insoluble lead and cadmium are filtered off and dissolved in dilute nitric acid. This procedure makes it possible to operate on a larger sample, and each 0.1 cc. of the potassium permanganate solution (0.568 gram to the liter) equals 0.001 per cent lead. Particular care must be taken not to dissolve the sample too fast, as there is danger of cadmium going into solution. In cases where lead alone is wanted solution may be hurried somewhat without impairing the accuracy. In this laboratory it is customary to run duplicate determinations on spelter, chiefly to guard against and detect any possible loss of cadmium.

The substitution of trichloroacetic acid, according to Fox, for any one of the mineral acids usually employed in separating cadmium and zinc, has been found advantageous, since it is not dissociated to the same extent as hydrochloric or sulphuric acids, and even concentrated solutions do not prevent the complete precipitation of cadmium. In the case of mineral acids the strength must be kept within narrow limits, as is well known. A slight excess prevents the precipitation of cadmium, while insufficient acid causes much zinc to be precipitated along

\* Eric John Ericson.

with cadmium and makes several reprecipitations necessary. By means of trichloroacetic acid only one reprecipitation is called for, unless it has been found that more zinc remained undissolved originally than was aimed at, as may be seen later.

**66. Method for Spelter.** Weigh out 19.2 grams of the sample and place in a No. 3 Griffin beaker. Add 50 cc. distilled water, and 50 cc. hydrochloric acid (1.10 sp.gr); warm gently and from time to time add more dilute hydrochloric acid until nearly all zinc is dissolved and only 1.0 to 1.5 grams remain, plus the insoluble lead and cadmium. Do not hurry the dissolution when cadmium is to be determined. A good plan is to add sufficient acid at the start and allow to stand over night. In the morning continue the addition of acid gradually and give it time until the proper stage has been reached. Filter off metallics and wash off thoroughly with hot water (not necessarily until all chlorides have disappeared).

Transfer whatever metallics are on the beaker by means of a fine jet of water. Now add 10 cc. concentrated nitric acid, boil until brown fumes cease to appear, and filter if traces of tin or antimony are indicated, which is seldom the case. If filtered and washed, the volume will probably be large enough. If not, add 75 to 100 cc. water, 30 cc. strong ammonia, and 4 to 5 grams solid ammonium persulphate. Should the lead be unusually high, say over one per cent, it is best to add the persulphate before the ammonia. This insures perfect oxidation even when lead runs high, but requires a standardization of the factor, as in the case of lead concentrates. Boil five minutes, allow the liquid to settle ten minutes, and filter while warm through double 11 or 12.5-cm. filters. Wash four times with hot ten per cent ammonia water, and five times with hot water.

Transfer filter with precipitate back into the beaker in which precipitation was made; add 25 or 50 cc. hydrogen peroxide solution (10-40 cc.  $\text{H}_2\text{O}_2$  U.S.P. strength to the liter), depending on the percentage of lead. Stir until dissolved, add 15 cc. nitric acid (1.20 sp.gr.) plus 100 cc. water, and titrate the excess of hydrogen peroxide by the standard permanganate solution.

For instance if 25 cc.  $\text{H}_2\text{O}_2$  blank require 60 cc.  $\text{KMnO}_4$  and the sample 28.5 cc., then the lead equals 0.315 per cent. The accompanying examples taken from practice show how closely the new method checks with the chromate determinations.

	Ericson Method, Per Cent.	Gravimetric as Chromate, Per Cent.
Refined spelter . . . . .	0.082	0.083
Refined spelter . . . . .	0.043	0.044
Prime western spelter . . . . .	0.530	0.538
Prime western spelter . . . . .	0.533	0.531

**67. Cadmium Determination.** For the determination of cadmium, evaporate the ammoniacal filtrate from lead until it is nearly neutral and zinc and cadmium commence to be precipitated, add 35 cc. dilute sulphuric acid (1:3) and boil down to about 150 cc. volume. Saturate with hydrogen sulphide gas, add 25 cc. water and warm. Sometimes it is necessary to add a few cubic centimeters of dilute ammonia to start precipitation. Allow the precipitate to settle, filter through double filters and wash. Test filtrate for cadmium, and if none is present reject it. Redissolve the cadmium sulphide, contaminated with zinc sulphide, in dilute hydrochloric acid (1.10 sp.gr.), and wash with water. If copper is present its sulphide remains insoluble on the filter. It may be ignited and weighed as copper oxide.

The filtrate containing cadmium and zinc chlorides is

neutralized with dilute ammonia, and trichloroacetic acid dissolved in water added until the precipitate is redissolved. Dilute to about 150 cc. volume and reprecipitate, adding hydrogen sulphide and water alternately. Settle, and determine by any one of the usual methods, preferably as sulphate or phosphate.

Should the color of the cadmium sulphide from the sulphuric acid solution be yellow, it indicates considerable zinc, which may be largely eliminated by boiling the solution of the mixed chlorides to expel hydrogen sulphide, adding sodium hydroxide in slight excess to precipitate cadmium, filtering, washing, and redissolving the cadmium hydroxide on the filter in trichloroacetic acid, diluting and reprecipitating with hydrogen sulphide, when a pure cadmium sulphide will be obtained. Should the duplicates not agree, precipitate the one giving the highest result, since it may still retain some zinc. If still too far apart, repeat the entire analysis.

**68. Uses and Valuation.** The uses for this metal are very few, and the total amount consumed annually cannot be much more than three tons of the metal, which sells for from \$1.00 to \$1.50 per lb.

## CHAPTER VII

### CALCIUM

**69. Ores.** The principal minerals containing lime are calcium carbonate, or calcite (in its impure forms, marble and limestone), calcium sulphate, or gypsum, calcium and magnesium carbonate (dolomite), and various silicates.

**70. Detection.** Decompose the substance with nitric and hydrochloric acids, add five cc. of sulphuric acid to precipitate the barium, add ammonia water to alkaline excess, and filter. To the boiling-hot filtrate add ammonium oxalate in solution; the formation of a white crystalline precipitate is evidence of the presence of calcium.

**71. Method.** Calcium is always reported as lime,  $\text{CaO}$ . In smelter work the "total lime" is that obtained by decomposition with the stronger acids. Certain silicates are not decomposed by acid treatment, and in such instances the term is a misnomer. "Available lime" in smelter work is that obtained when only acetic acid is used for the decomposition. This determination is called for to escape payment for any lime occurring as calcium fluoride, it being asserted that lime in such combination is not available for slag formation. By this determination a portion of the lime in certain dolomitic ores is lost by imperfect decomposition, together with some lime occurring as sulphate. The technical analyst is not, however, concerned with these matters. The smelter contracts for the purchase of ores are made for "total lime" or "available lime," and it is the duty of

the analyst to employ the methods of decomposition provided by smelter usages.

**72. Decomposition.** A half gram of the pulp is taken, and if "total lime" is required the decomposition is made in a beaker with five cc. of concentrated hydrochloric acid and an equal amount of nitric acid. Heat is employed to complete the decomposition. Ammonia water is then added to alkaline excess, with ten cc. of bromine water to precipitate the manganese. The bulk of the liquid should be 200 cc. to insure solution of all lime occurring as calcium sulphate. The precipitated oxides are filtered off and, after washing with hot water, the filtrate is set aside. The oxides are then dissolved in five cc. of concentrated hydrochloric acid and precipitated with ammonia water and the addition of five cc. of bromine water, then filtered, and the filtrate and washings added to the first filtrate, which is then brought to a boil before the precipitation as oxalate.

**73. Available Lime.** One-half gram of the ore is placed in a six-ounce flask, moistened with water, ten cc. of strong acetic acid added, and boiled nearly to dryness. A mixture of equal parts of water and acetic acid is made, and thirty cc. of it added to the flask and boiled for several minutes. Filter hot and wash with hot water. Make the filtrate alkaline with ammonia and filter off the iron hydroxides, when it is ready for precipitation with ammonium oxalate.

**74. Precipitation.** The lime is precipitated as oxalate by first adding three cc. of glycerin; then thirty cc. of a saturated solution of ammonium oxalate are added to the boiling hot solution of lime, and boiled for half an hour, when the precipitate, which is free from magnesium oxalate, settles, and is filtered off through a closely woven filter (11 cm.). The precipitate is washed thoroughly with boiling hot water to wash out all the excess of ammonium oxalate.

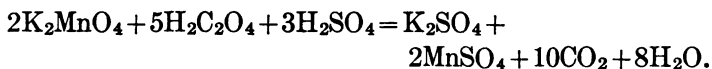
It frequently happens that analysts are troubled by the calcium oxalate running through the filter, particularly if they pour fresh solution through the filter before all the previous addition has passed through. All trouble from this source is obviated if the analyst will allow the end of his stirring rod, when pouring, to be beneath the surface of any liquor remaining in the funnel. Why this is so, I do not know, but the fact is well enough known.

If much magnesium is present, a portion of it is apt to be precipitated with the lime as oxalate. The amount of this is so small, particularly when glycerin is added, that there is no need to redissolve the precipitate and again precipitate with ammonium oxalate; but, if there are soluble barium compounds, considerable error may be caused if the precaution is not taken to remove the bulk of the barium by the addition of five cc. of sulphuric acid to the original solution previous to precipitation with ammonia water. If this is done then the analyst must be certain to see that any calcium sulphate found is washed out from the precipitate of barium sulphate.

**75. Titration.** Fifty cc. of pure water are placed in a 400-cc. beaker and seven cc. of concentrated sulphuric acid added. The calcium oxalate on the filter is washed into this mixture with a strong jet of water, the filter being opened out to insure removal of all the precipitate. The solution should have a bulk of about 200 cc.; it is heated to near boiling, and while hot is treated with a standard solution of potassium permanganate. The solution used for the titration of iron is generally used, and its strength is determined by multiplying the iron factor with 0.5017 to obtain the CaO factor.

**76. Chemistry.** The calcium oxalate is decomposed by the sulphuric acid, forming free oxalic acid. The

reaction of the oxalic acid with the potassium permanganate is as follows:



The results by this method are accurate, and give all of the lime, except when the conventional acid treatment does not completely decompose the pulp.

**77. Gravimetric Method.** The precipitate of calcium oxalate, derived by precipitation with ammonium oxalate, may be quickly dried and placed with the filter in an annealing cup and ignited in a hot muffle. So soon as the ignited residue is sufficiently cooled to handle, it is dusted out on the scale pan and weighed as CaO. The heat required to drive off the last of the CO<sub>2</sub> is moderately high, and it is best to begin the ignition in the front part of the muffle, shoving it back into the hotter part after the oxalic acid is decomposed.

**78. Valuation.** The western smelters pay for lime always, when there is five per cent, or more, in the ore, at the rate of from four to ten cents per unit, the average rate being five cents per unit. The rate varies with the desirability of the ore, and the need of the smelting plant for lime to produce its slags. As a general rule the smelters have to buy more or less pure limestone. The price paid for this limestone varies greatly, according to the local conditions governing the cost of mining and delivering the flux. It is impossible to give a definite amount for this valuation, but it is usually in the neighborhood of one dollar a ton. The above applies to the carbonates of lime.

In the case of fluorspar, there is a special demand on the part of the makers of iron, particularly in open hearth



work. Large quantities of it are also used in the manufacture of glass. Ground fluorspar sells for from \$8.00 to \$15.00 per ton; the lump for from \$4.00 to \$9.00, and the gravel for from \$2.00 to \$6.00 per ton; the prices varying according to purity.

## CHAPTER VIII

### CHROMIUM

**79. Ores.** Chromite, or chrome iron ore, is widely distributed and occurs in considerable quantity. Chromium is used in the making of chrome steel and is introduced as ferrochromium. Pure metallic chromium is but seldom seen.

**80. Detection.** Mix a portion of the finely pulverized ore with three times its volume of dry sodium peroxide and fuse on a piece of platinum foil. Dissolve the fused mass in a small quantity of water, making faintly acid with acetic acid, and add a few drops of solution of lead acetate. If a yellow precipitate forms, chromium is present.

**81. Requirement.** Chromium mineral substances are difficult of decomposition, and it is highly essential that the mineral should be reduced to the finest possible degree of subdivision. The western assayer is seldom called upon for a chromium determination.

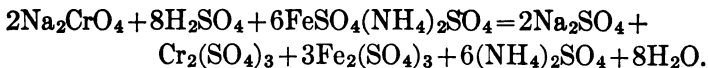
**82. Decomposition.** One-half a gram, or more if the amount of chromium present is small, is intimately mixed with ten times its weight of sodium peroxide and placed in a nickel, or copper, crucible. Heat gently until fused, and keep in a fused condition for from ten to fifteen minutes. The fused mass is then cooled and placed in a No. 3 casserole, covered with water and boiled to dissolve the sodium chromate, as well as to decompose all of the sodium peroxide. Filter off the residue, wash it with hot water, and set the filtrate aside. The residue on the

filter paper should be treated with hydrochloric acid, and if it fails to completely dissolve it is advisable to fuse the undissolved portion again in sodium peroxide, since it may be partly composed of undecomposed chromates, adding the filtrate obtained from the second fusion to the first filtrate.

**83. Titration.** The solution will be yellow in color if chromium is present. It is acidified with sulphuric acid, diluted to 700 cc., and allowed to cool to room temperature, when a weighed amount of ammonio-ferrous sulphate is added, so there will be an excess of ferrous salt. One gram of the ferrous salt will be sufficient for 0.04427 of chromium. When there is an excess of ferrous salt, the yellow color of the solution will have disappeared. So soon as there is an excess of ferrous salt, determine the amount by titration with permanganate solution. Deduct this amount from the weight of iron in the ammonio-ferrous sulphate added, by which the weight of ferrous iron oxidized by the chromium will be found. This weight multiplied by 0.31067 will give the weight of chromium in the pulp taken, from which the percentage is calculated in the usual way.

If the permanganate solution has a strength of one cc. equal to 0.005 of iron, then 28.5 cc. of the permanganate will equal one gram of ammonio-ferrous sulphate, provided it is chemically pure.

#### 84. Reactions.



**85. Uses and Valuation.** The demand for chromium in the United States is chiefly supplied by importations from Australia, Greece and Turkey. The metal is used for

the manufacture of chromium salts and ferro-chromium alloys.

Ore carrying fifty per cent chromium and over is worth, f.o.b. New York, from \$14.00 to \$20.00 per ton of 2240 lbs.

## CHAPTER IX

### COPPER

**86. Ores.** The most important ores of copper are native copper; cuprite; melaconite; malachite; azurite; chalcopyrite; bornite; chalcocite; chrysocolla and tetrahydrite. These minerals occur alone, but are more frequently associated with each other as well as with minerals of the other metals.

**87. Detection.** Heat a small portion of the pulverized mineral in a test tube, or casserole, with a small amount of hydrochloric and nitric acids. In a few minutes partial decomposition will occur, sufficient to determine the presence of copper unless in very small quantities; then add an equal volume of water and an excess of ammonia water; on allowing the precipitated matter to settle, a blue colored liquid will be found if copper is present. On acidifying the liquor with hydrochloric acid and immersing a clean piece of iron in the solution, the iron will be covered with a reddish deposit of metallic copper.

**88. Methods.** Copper is determined by either one of three methods, called the iodide, cyanide and electrolytic. The three methods, if each be carefully executed, are of equal value, and will give the same results on the same pulps. The possibilities for error are greatest in the electrolytic method, and while I personally prefer the cyanide method, being equally as accurate as the others, besides being quicker and less expensive to make, I find that the iodide method is most certain, the end reaction being easier to distinguish than the cyanide end-point.

I find many persons, possibly because of some defect in eyesight, totally unable to detect with reasonable certainty the end reaction of the cyanide method.

While most analysts omit the precipitation of copper on aluminum, particularly when the electrolytic method is employed, I never omit this treatment, and believe it adds largely to the accuracy of either method. A great many analysts will take exception to this statement, but it is an opinion based upon my own experience. Accordingly, I recommend the following treatment down to resolution in nitric acid after precipitation on sheet aluminum, no matter what method may be followed.

**89. Decomposition.** Place 1 gram of the pulp in a No. 2 casserole and cover it with from 5 to 7 cc. of concentrated nitric acid; cover the casserole with a watch glass, and allow the acid to act for 10 minutes at a temperature not to exceed 40° C.; then add 3 cc. of strong hydrochloric acid and allow the assay to stand for about 20 minutes. Should there be particles of unoxidized sulphur floating about in the solution, one gram of crystals of potassium chlorate may be added cautiously. Then evaporate to dryness on a hot plate, taking care that there shall be no spattering and keeping the casserole covered during the evaporation. Certain siliceous ores are likely to be troublesome in the matter of spattering, and it may be necessary to make the evaporation on a water bath, or in an air bath. Evaporate to hard dryness, then add five to seven cc. of concentrated sulphuric acid, and heat until strong fumes of sulphuric oxide begin to come off copiously. Remove from the hot plate and, after cooling somewhat, cautiously add cold water, being careful to avoid any loss of liquid by the spattering caused by the intense heat caused by the addition of the water to the concentrated sulphuric acid. Allow to stand for a few minutes, then filter through

a 3-inch filter and wash thoroughly with hot or cold water, collecting the filtrate in a 150-cc. beaker. The bulk of the filtrate after washing should not be more than 100 cc. nor less than 60 cc.

**90. Precipitation on Aluminum.** Place a strip of sheet aluminum  $\frac{1}{16}$  of an inch in thickness,  $\frac{1}{2}$  to 1 inch in width and 2 or 3 inches in length, and bent in the form of a V, in the beaker; place this on the hot plate and boil until the solution becomes colorless, which will usually be complete in less than 15 minutes of boiling. *All* of the copper will be precipitated together with any other metals present which are precipitated by aluminum from their acid solutions. Remove the beaker from the hot plate and immediately fill it up with cold tap water; stir the aluminum with a stirring rod, which will usually detach all of the copper; remove the aluminum and place it on the watch glass used to cover the beaker; decant off the solution, after allowing the precipitated metals to settle, and wash once by decantation. If the analyst has followed directions and evaporated to dryness he will always find *all* of the copper is precipitated. The presence of small amounts of hydrochloric and nitric acids, in the free state, may prevent complete precipitation, but if directions are followed they will be absent. Copper will not redissolve in dilute sulphuric acid. Sometimes the metallic precipitate is so light, usually due to the precipitation of other metals with the copper, that it cannot be handled by decantation with safety; in that event the solution should be decanted through a filter. The metallic precipitate may contain cadmium, lead, mercury, bismuth, antimony, arsenic, tin and silver.

**91. Dissolving the Copper.** Measure off five cc. of concentrated nitric acid, carefully drop a little of it on the aluminum to dissolve any metal adhering to it, and add

the remainder to the metallic residue remaining in the beaker and shake it to dissolve it. Then wash the watch glass and aluminum into the beaker, being careful not to make the bulk unduly large. The copper is now ready to be determined by the cyanide, iodide, or electrolytic method, with the modifications peculiar to successful working of the method selected.

#### CYANIDE METHOD

**92.** The nitric acid solution is made alkaline by the addition of ten cc. of concentrated ammonia water, which will make a blue solution, almost perfectly clear, except for small amounts of precipitated aluminum hydroxide. The solution is then made up to a constant bulk; about seventy-five cc. is most desirable, using cold water. The solution is then set aside to cool to room temperature.

**93. Titration.** The cooled solution is transferred to a clean porcelain casserole of about 200 cc. capacity, and a standard solution of potassium cyanide is run in from a burette, with constant stirring, until the blue coloration disappears; the solution is then poured back into the original beaker and returned to the casserole, washing out the last portions of liquors in the beaker by the water jet. In the titration the blue color passes away, and near the end there is a pale purplish tint; some analysts stop at this point but I continue until the tint disappears. The analyst determines for himself the end-point he will adopt, and always stops at it when standardizing, or running on a pulp. The cyanide may be run in rapidly until near the point, when it must be cautiously added, drop by drop.

**94. Standardizing.** Dissolve the purest potassium cyanide available, so that one cc. will be equal to 0.005



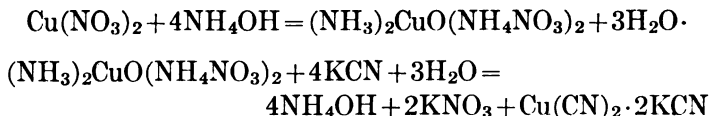
gram of copper, or one cc. of the solution will correspond to one-half of one per cent of copper. About twenty grams to the liter will give the desired strength, or nearly so.

The solution should be allowed to stand over night, if convenient, before determination of its strength, and it is usually advisable to decant the solution into the storage bottle. The storage bottle should be of dark-colored glass, and it should be kept away from direct sunlight as much as possible; it should be restandardized at least once in every week, as it slowly loses its strength. To standardize, weigh out from 0.1 to 0.2 gram of pure metallic copper into a beaker, cover with 7 cc. of concentrated nitric acid, and dissolve the copper, then add 20 cc. of water and 10 cc. of concentrated ammonia water; dilute with cold water to 75 cc., and when it has cooled to room temperature titrate with the cyanide solution, as previously described. The weight of copper divided by the cc. of solution used will give the strength of the solution. When accuracy is desired, it will be found advantageous to standardize while making the assay, using a weight of copper roughly corresponding to the per cent of copper in the ore.

The important factors in good work with this method are constant volume, constant temperature and regularity of adding the cyanide when near the end point. Of the metallic substances liable to be present, owing to their precipitation on aluminum foil, silver is the only one that will consume cyanide, and it may be neglected, as nearly all the silver present in the pulp will be precipitated by the use of hydrochloric acid in making the decomposition of the pulp.

**95. Chemistry.** The method is based upon the formation of a bluish-colored salt of ammonium and copper when ammonia water is added in excess to a solution of a

copper salt; and on the addition of potassium cyanide to such a solution colorless double cyanides of copper and potassium are formed. together with ammonium hydroxide and potassium nitrate:



The above reactions are commonly given, but it must be borne in mind that they are partly affected by concentration, temperature, and especially by the excess of ammonium salts.

**96. Varying Bulk.** In these and the following studies a solution of twenty grams of copper was made with 100 cc. of concentrated nitric acid and diluted to one liter. The same solution of cyanide was used in all experiments. In studying the effect of varying bulk, ten cc. of the prepared solution was taken, to each of which was added ten cc. of concentrated ammonia water and such amounts of water as necessary to give the required bulk. The titrations were made at room temperature, about 18 to 19° C.

Bulk, cc.....	20	30	50	100	200
Cyanide used, cc.....	40.3	40	40	39.9	38

Large variations in bulk lead to errors, and a bulk of from 50 to 100 cc. seems most advantageous.

**97. Varying Ammonia.** Ten cc. of the solution were taken, the specified amounts of ammonia water added and the bulk brought to 100 cc., and the temperature 18° C.

Cc. of ammonia.....	10	15	20	30	Just sufficient to dissolve copper
Cyanide used, cc. ....	40	40.8	41.4	42.6	
					39.9

**98. Varying Copper.** Ten cc. of ammonia water were added except when twenty cc. of the prepared copper solution were employed, when it was found necessary to add more of the ammonia water to redissolve the copper. The other conditions were as before.

Cc. of copper solution.....	1	5	10	20
Cc. of cyanide used.....	3.8	19.9	40	80

I interpret these results and those of varying the ammonia as showing that the cyanide consumed is directly proportional to the copper, but varying with the excess of ammonia over what is just necessary to dissolve the precipitated copper to a clear blue solution.

**99. Varying Temperature.** All conditions uniform except as to temperature.

Temp. at titration.....	18° C.	25° C.	30° C.	35° C.	40° C.
Cc. of cyanide used.....	40	39.8	39.7	39.4	39.1

**100. Varying Ammonium Nitrate.** Uniform conditions observed with additions of indicated amounts of ammonium nitrate.

Grams ammonium nitrate.....	1	2	4	8	16
Cc. of cyanide.....	40.1	40.1	40.1	40.6	41.5

**101. Effect of Certain Metallic Salts.** In these experiments soluble salts of the metals were added so that the weight of metal should be approximately as stated.

Weight of metal in grams ....	0.02	0.04	0.08	0.16
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#### CC. OF CYANIDE CONSUMED

Aluminum.....	40	40.1	40.0	40.1
Silver.....	41.0	41.9	44.1	47.8
Cadmium.....	40.0	40.1	40.1	40.1
Nickel.....	40.4	40.8	41.7	43.0
Lead.....	40.1	40.0	40.1	40.1
Arsenic.....	40.1	40.1	40.1	40.1
Antimony.....	40.0	40.1	40.0	39.9
Bismuth.....	40.0	40.0	39.9	39.9

**102. Quick Cyanide Method.** When approximate results with one-half of one per cent are admissible the cyanide method may be abbreviated. Decompose the ore as previously described and evaporate to dryness. Then add ten to fifteen cc. of concentrated ammonia water and filter through a three-inch filter, washing with cold water. Titrate in the regular manner. This method is particularly well adapted to those instances when assays have to be made in the field.

#### IODIDE METHOD

**103.** The iodide method has secured a very high place in the estimation of technical chemists, and it is owing to the labors of Mr. A. H. Low, of Denver, that it has been so well developed. The method described here is practically Low's method, differing from his instructions in that it is unnecessary to add hydrogen sulphide gas to precipitate the small amounts of copper which he claims remain in solution after the precipitation on aluminum foil. Complete precipitation is secured on aluminum by strictly following the instructions given in 89 and 90.

**104. Preparation of Solution.** The nitric acid solution of the copper of 91 is treated with five cc. of bromine water, or more if necessary to impart a permanent tinge to the solution, and boil until the fumes of bromine are removed, for the purpose of driving off all nitrous fumes. Remove the solution from the hot plate, add ammonia water to slight excess, and then acidify with acetic acid; one to two cc. of the glacial acetic acid are usually enough when the ammonia has been added cautiously. If there is much arsenic in the solution, a precipitate of cupric arsenate is formed, and in that event enough additional acetic acid will have to be added to hold it in solution. Cool

the solution to room temperature and add an excess of potassium iodide (three grams will usually suffice); on the addition of the iodide, cuprous iodide will be precipitated together with free iodine, making a brownish-colored deposit. The bulk of the liquid should be between 150 and 200 cc., and when cooled to room temperature it is ready for titration.

**105. Titration.** A standard solution of sodium thio-sulphate is then run into the liquid until the brownish coloration has almost disappeared, stirring constantly with a stirring rod, or shaking. Then add ten cc. of starch liquor when the solution will become blue, or even black, in color. Then complete the titration drop by drop, until the blue color disappears, even the faint lilac tint, which comes at the end. The end-point is comparatively sharp, and most analysts find it easier to distinguish than the end reaction of the cyanide method. This sharpness is the only real point of superiority in the iodide method. The strength of the standard, multiplied by the number of the cc. used, gives the weight of the copper in the solution, from which the percentage of the copper is easily calculated.

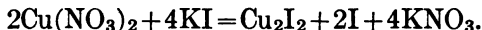
**106. Standardizing.** Dissolve about nineteen grams of thiosulphate in one liter of distilled water to make a solution each cc. of which will be equivalent to about 0.005 gram of copper. The solution is very stable and does not need to be frequently standardized.

The starch solution is made by boiling one gram of starch with 200 cc. of distilled water until a paste is formed; it is then diluted to 300 cc., when it is ready for use after cooling to room temperature. It must be freshly prepared every two weeks.

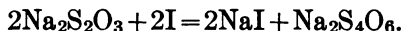
The thiosulphate solution is standardized by dissolving 0.1 to 0.2 gram of pure copper foil, placed in a beaker,

with 7 cc. of concentrated nitric acid. After solution, boil for a few minutes, add 5 cc. of bromine water, and boil until all of it is volatilized. Remove from the hot plate, add 25 cc. of water and then 8 cc. of strong ammonia water, or until it is in slight excess; then boil again to remove the excess of ammonia. Then make acid by the addition of 2 cc. of glacial acetic acid, dilute to 150 cc., add 3 grams of potassium iodide, cool to room temperature, and titrate as described in 105. The weight of copper divided by the number of cubic centimeters of thiosulphate consumed gives the strength of the standard solution.

**107. Chemistry.** On the addition of the potassium iodide, potassium nitrate is produced, remaining in solution and cuprous iodide mixed with free iodine is precipitated as follows:



On the addition of the thiosulphate the free iodine is converted into soluble sodium iodide, as shown by the following equation:



**108. Varying Temperature.** The solution must be kept cool, or at room temperature, otherwise the delicacy of the starch reaction with iodine is destroyed.

**109. Varying the Potassium Iodide.** There must be enough potassium iodide present to precipitate all of the copper and to dissolve the free iodine. One gram of copper requires five grams of potassium iodide, so that by using three grams there will always be sufficient, except in very exceptional cases. An excess of as much as ten grams of the iodide does not disturb the accuracy of the titration.

**110. Varying the Bulk.** Varying the bulk of the solution between 100 and 400 cc. does not apparently disturb the result.

**111. Varying the Acetic Acid and Copper.** Experiments show that the consumption of thiosulphate is directly proportional to the amount of the copper present; likewise it has been found that varying the acetic acid in excess from one to twenty cc. does not disturb the results.

**112. Varying the Sodium and Ammonium Acetates.** The effect of these salts was determined by having all of the conditions uniform, except by adding varying weighed quantities of the two salts.

Grams of salt added . . . .	0	1	2	4	8
Sodium acetate . . . . .	40	40	40.1	39.6	37.2
Ammonium acetate . . . . .	40	40	40.2	39.9	38.2

**113. Effects of Various Metallic Salts.** 0.1 gram of soluble salts of arsenic, antimony, lead, tin, silver, cadmium, zinc, aluminum and bismuth were added to aliquot parts of a prepared solution of copper, and titrated under uniform conditions. They all were found to be without effect except that in the cases where lead, or bismuth, was present it was difficult to distinguish the end-point, usually requiring more cubic centimeters of the thiosulphate solution. When ferric chloride was added the consumption of thiosulphate was increased by about ten per cent, owing to the fact that iodine is liberated by the ferric acetate.

## ELECTROLYTIC METHOD

114. The solution of copper nitrate as prepared in 91 is diluted somewhat, 10 cc. of nitric acid added, and diluted to 150 cc. The solution is placed in a tall and narrow beaker; a platinum cylindrical cathode, weighing about 10 grams, previously thoroughly cleaned and accurately weighed, is immersed in the solution, and an anode of coiled No. 18 platinum wire, weighing about six grams is likewise immersed, so that it will be inside, but not touching the bottom of the beaker. A suitable battery, or other convenient source of electric current, is used to give a current of a tension of between two and three volts, with a flow of about 0.7 ampere. The cathode is connected with the zinc, or negative, pole, and the anode with the other. The solution is kept at ordinary room temperature and the current allowed to pass until deposition is complete, requiring five to six hours. In using this method it is customary to start the deposition late in the evening and permit the current to act through the night. When the deposition is completed, the beaker is lowered and a beaker filled with distilled water is quickly put in its place; in a few minutes it is removed, the cathode is washed with alcohol, which is allowed to drain off, and after drying at 100° C., it is weighed. The increase of weight of the cathode allows the easy calculation of the percentage of copper. The copper should be firm and bright red in color, in which event the determination will be accurate.

The precipitation of copper on aluminum previous to its determination electrolytically I have found more satisfactory than the method usually recommended. It is true that arsenic, antimony, bismuth and silver are precipitated on aluminum, and will be in the solution



to be electrolyzed. The silver is, however, almost completely precipitated in the earlier treatment by the use of hydrochloric acid, and it cannot affect the results sensibly. The arsenic and antimony are not deposited by the electric current of the strength recommended, in the presence of so much nitric acid. The bismuth is almost completely precipitated, likewise mercury, if present, consequently they must be removed to secure an accurate determination. Mercury is not at all likely to be met with in nature associated with copper, and bismuth is only found occasionally, most commonly in mattes. Bismuth causes the copper to darken, or gives it a grayish color, even when less than one-half of one per cent of it is present. The quickest way to correct it is, after the deposition redissolve the precipitated copper with a minimum amount of nitric acid, add ammonia in slight excess which precipitates the bismuth, filter it off, and after acidifying the filtrate with nitric acid and diluting it properly, reprecipitate the copper with the electric current. When bismuth is known to be present, it may be removed at the time the copper is redissolved in nitric acid, after precipitation on aluminum, by making alkaline with ammonia, filtering the precipitated bismuth, reacidifying the filtrate and proceeding in the regular manner. If mercury is present in the ore, or pulp, the aluminum method cannot be recommended, and the original solution from the pulp must be precipitated with hydrogen sulphide gas, according to the electrolytic method as generally followed by most analysts.

Owing to the physical characters of the sulphide precipitates they cannot be handled without some slight loss; for this reason, as well as the other disagreeable features connected with the use of hydrogen sulphide gas, I always try to avoid its use. The following description

is given, because it is the method usually employed, and because the method described by me is not adapted to the determination of copper in the presence of mercury.

**115. Usual Method by Electrolysis.** One-half a gram or one gram of the pulp is decomposed as described in 89. The filtrate from the insoluble residue is diluted to 300 cc. and a current of sulphureted hydrogen gas is passed through until the supernatant liquid, on standing, is perfectly clear. Filter off, using a filter pump, and wash thoroughly with hydrogen sulphide gas water. Rinse the precipitate back into its beaker, without removing the filter, and add twenty cc. of a strong solution of potassium sulphide, heat to boiling, allowing to settle, and decant through the original filter. Repeat the removal of the arsenic and antimony sulphides by fresh addition of potassium sulphide, filter off through the original filter, and wash with water containing potassium sulphide. The precipitate is rinsed back into the beaker, and if it is desired to remove any bismuth that may be present, the liquid is made alkaline with ammonia water, three grams of potassium cyanide are added, and the whole gently warmed, dissolving the copper sulphide, and leaving the bismuth sulphide as the residue which is filtered off; ten to fifteen cc. of strong nitric acid are added and the solution boiled until decomposition is complete, when it is filtered off and electrolyzed as described in 114.

**116. Remarks on the Three Methods.** The electrolytic method is reputed to be the most accurate method for the determination of copper, but the only reason I can find for that belief is that the materials in that method cost more than in the other two methods. For all analysts know that if the electrolytic method is followed out properly, so as to eliminate all metals that would be precipitated with the copper by the electric current, then

the copper found is always less than the actual amount of copper in the pulp. This loss is due to the repeated handlings of the precipitates, and is not alone peculiar to the copper method. On the other hand, if care is not taken to remove the interfering substances, the results will be too high. These facts are well known to all analysts of experience. I have found that the electrolytic method is much improved by omitting the hydrogen sulphide gas treatment and precipitating on aluminum foil instead. With this modification I consider one method as good as the others, and give the palm to none. Local considerations may make one method more desirable than the others. If very many copper determinations have to be made daily, the electrolytic method will probably permit the handling of the greatest number, certainly more than by the iodide method. The iodide method takes a longer time than the cyanide method, but it is to be recommended as the best method adapted for general use, the end-point being always easy to distinguish. Personally I prefer the cyanide method, and if the analyst is capable of sharply determining the end-point, it is equal to any other method proposed for the determination of copper. It is the quickest and most economical method, and with it I believe the analyst can handle as many determinations daily as can be handled in the most extensively equipped electrolytic laboratory.

**117. Valuation.** The smelters pay for all the copper shown, by wet analysis in the ore, less 1.3 per cent, said to represent the loss of copper in the slag. When the per cent of copper is less than 13 per cent, it is customary to pay for 90 per cent of the copper content, instead of deducting the 1.3 per cent.

The price of casting, or electrolytic, copper in New York is taken as the basis of settlement, from which is

deducted from two to as much as six cents according to the character and desirability of the ore, the needs of the smelters, the sizes of the shipments, and other factors not clearly understood by the seller, but based upon difficulties found by the smelters in smelting the ores.

The following equation represents the practice:

Per cent copper in ore  $\times 20 \times$  (price of casting copper, N. Y., in cents per lb. less 2, or 3, or 4, or 5 cents)  $\times 90$  per cent, minus smelting charges (from \$3.00 to \$9.00 per ton).

**118. Uses.** Copper is employed in large quantities for the manufacture of wire, most of which is employed in the manufacture of electric machinery and for conducting electric currents. It is also employed in the sheet form for roofs and sheathing sea-going vessels. The salts of copper are also of importance in the arts. The alloys of copper are very numerous and of great practical utility.

## CHAPTER X

### GOLD AND SILVER

#### CRUCIBLE PROCESS

**119.** Gold ores are always determined by the use of the crucible process, and most silver ores should be assayed by the same process, which consists in mixing from fifteen to thirty grams of the ore fine enough to pass a 120-mesh sieve, with proper quantities of soda, pearl ash, borax glass and litharge to form, on heating, a fused mass composed of "slag" containing the earthy impurities of the ore and a lead button of sufficient size to collect all of the gold and silver in the ore.

**120. Fluxes.** In western assay offices there is usually kept on hand a special mixture of soda, litharge and borax glass with an amount of reducing material sufficient to produce a lead button weighing from fifteen to twenty grams with the character of ores usually assayed. This flux is of variable composition, varying principally with the character of the common ores of the locality, and partly from the varying ideas of individual assayers. Some of these individual variations are considered of great importance by their originators, but I believe that the only essential conditions are: sufficient soda, or pearl ash, to slag off the earthy impurities; enough borax glass to help dissolve the metallic oxides and to make the slag fluid enough to permit the lead reduced from the litharge by the action of the ore, or the action of a suitable reducing reagent, to shower through the mass and collect

every particle of gold and silver in the pulp treated. There should be an excess of litharge, so that part of it should go into the slag, increasing its fusibility. With these essentials and a good hot fire, there is never any trouble in securing good results.

If sulphides are present in the ore, wire nails must be used to desulphurize, and all antimonial and arsenical ores, as well as zinc ores, give better results if the pulp is roasted previous to mixing with the flux. In ordinary routine work the assayer seldom resorts to trial charges to determine the reducing or oxidizing power of the ore. By experience he learns to tell by simple inspection what character of flux is needed, and it is astonishing to one not familiar with the work of assayers to see how seldom they err in their judgment.

There are occasions when the assayer resorts to the trial assays, when some new ore gives him trouble when he uses his regular flux. He then resorts to the methods given in so many standard texts.

Silica must sometimes be added to certain ores to secure good decompositions. The reducing agent preferred by me is argols, but flour is probably most commonly used. The requisite amount of flux is placed in a crucible of convenient size, a 20-gram crucible being generally used for a charge when half an assay ton of pulp is employed. The pulp is then weighed out and mixed with the flux in the crucible, with the aid of a spatula. Any special variations in the flux are then added and intimately mixed with the charge. Nails are added if sulphides are present, and a thin layer of flux is then placed over the top of the charge, followed by a layer of common salt, or borax glass, as a cover. I prefer borax glass since it helps make a cleaner pour. The crucibles are then placed in a hot muffle and the door

is closed. Fusion soon begins and in about thirty minutes, if the fire is right, the fusion will be complete, when the crucibles are withdrawn, the nails removed with the forceps, and their contents carefully poured into the heavy iron molds, used for this purpose. The crucibles may be used repeatedly, until the sides become so thin that the charge is likely to eat its way through. But no crucible should be used a second time if the slags have not poured well. In a good fusion the amount of silver that would remain in the small amount of slag lining the crucible would not salt the result sensibly. On cooling, the slag is broken off from the button and it is hammered into the form of a cube to make it ready for cupellation.

The following mixtures make excellent universal fluxes and may be made up in large quantities to be used as needed. The quantity mentioned is to be used with half an assay ton of ore.

	My Mixture, Grams.	Aaron's Flux, Grams.	Brown's Flux, Grams.
Soda.....	13	13	45
Pearl ash.....	13	....	15
Borax glass.....	9	13	15
Litharge.....	27	27	45
Argols.....	3	....	....
Flour.....	....	1.5	....
Charcoal.....	....	....	0.6
Silica.....	As needed	As needed	3.0

Most of the ores coming to my office are oxidizing in character, and my charge is varied slightly by special additions as I think they are needed. The following are well adapted for the special kinds of pulps. They are based upon using half an assay ton of the ore.

	Silicious, Grams.	Limey, Grams.	Iron Oxides, Grams.	Zincy, Grams.	Sul- phides, Grams.	Coppery, Grams.
Soda.....	60	30	20	20	20	20
Pearl ash.....	..	20*	20	20	40	20
Borax glass.....	5	20	10	10	10	15
Litharge.....	50	30	30	45	50	75
Argols.....	2	3	7	3	1	7
Silica.....	..	3	5	2	..	..
					Nails	

The amounts of reducing agents mentioned will usually give a lead button between fifteen and twenty grams in weight, except in the case of coppery ores where a lead button should be gotten that will weigh about fifty grams, afterwards scorifying it to about eighteen grams before cupelling it.

The muffle should be at a good bright heat before any crucibles are introduced, so that the fluxes will be active and working on the gangue before the reducing agent begins to shower the lead. If the lead is reduced too quickly there will be loss of silver and gold, no matter if the crucible later pours completely. *Keep up the heat.*

In crucible work it will sometimes be found that the lead does not settle well through the matte, due to the fact that the muffle is not sufficiently hot. This can be remedied in but one way—*increase the heat.*

In assaying for gold and silver I prefer to use litharge so free from silver that it is unnecessary to make any correction. In assaying for gold I always add a small piece of silver, to insure a button large enough to be readily seen and transferred to the parting vessel. I sometimes find a larger amount of gold when I use the silver than when I omit it.

**121. Telluride Ores.** The difficulties in assay of tellu-



ride ores are partly due to the tellurium, and also owing to the fact that they are usually high grade, rendering it more difficult to accurately and uniformly sample. The higher the grade of the ore the more finely it should be crushed, and many of the troubles with telluride ores may be nearly eliminated by crushing to pass a 200-mesh sieve. This is the first essential precaution in the assay of tellurides; the next is to use a large quantity of litharge, 120 grams to half an assay ton of pulp, and enough argol to give a lead button of fifty grams which can be scorified down before cupellation.

My personal experience with the assay of telluride ores has not been as great as that of many assayers, and I am pleased to note that Prof. Lodge in his assaying notes confirms my own conclusions.

#### SCORIFICATION

**122.** This, the simplest, is an oxidizing process especially adapted for ores containing zinc, copper, arsenic and antimony.

The operation consists in heating about three grams of ore in a scorifier with from 45 to 80 grams of granulated lead and from one-fourth to five grams of borax glass. For some ores silica is also used, and in some instances even litharge, or soda, may be advantageously employed.

The usual scorifier employed is two and one-half inches in diameter. One-half the amount of lead to be employed is placed in the scorifier and spread over the bottom. The ore is then weighed out. One-tenth of an assay ton is used of the ore, and this is mixed with the lead; the other half of the granulated lead is then poured over the mixture, and one-fourth of a gram of pulverized borax glass is then placed on top of the mass, but to one

side of the scorifier, near the contact line of the charge with the scorifier.

The operation is conducted in the muffle, which should be very hot before the charges are introduced. As soon as the charges are placed in the muffle, the door should be closed and kept closed until the lead has well melted, at which time the ore will be found floating on the melted lead, of which there should be bright spots appearing.

During the second stage of the process the door should be open, and there should be a strong volume of air passing through the muffle. During this stage litharge is formed, which unites with the silicious contents of the ore, forming a very fusible slag which flows off to the side of the scorifier; the metallic oxides dissolve in the borax glass and pass into the slag. Zinc, antimony, arsenic and sulphur are oxidized and volatilized to a great extent, but a portion of them enter the slag.

During the operation, the silver, gold and copper alloy with the melted lead and, if the operation is properly conducted, the slags will be almost free from silver and gold. Some ores will require an addition of pulverized silica in order to effect a perfect decomposition, and it may also be necessary to add more borax glass to insure a fluid slag. In all cases where more than one-fourth of a gram of borax glass is needed, it should be added cautiously after the scorification is well begun. Its earlier addition is apt to interfere, more or less, with the oxidation of the charge, and prevent complete decomposition of the ore. If the slag does not flow freely, the addition of a small amount of potassium, or sodium, carbonate, will help.

In the event that the eye does not form well, it is an indication of too little heat, or too little lead. More lead may be added, and if the operation does not then

proceed better it is an indication of too little heat, the effect of which will be to give low results, particularly in silver.

The oxidization process ends when the slag formed entirely covers the lead. The door should then be closed and kept closed for about five minutes to produce perfect fluidity of the charge, after which the scorifiers are withdrawn and poured into molds which are usually lighter, as well as smaller, than those employed for pouring crucible charges. The molds should be clean, and there is no advantage in lining them with chalk or iron oxide. The scorifiers should be free from lumps and ridges of slag, and are thrown away after once using. When sufficiently cold, the slag is broken off the lead; the button is hammered into the form of a cube to free it from the slag, and then placed in its proper position in the cupel tray. The lead button should not weigh more than twenty grams, nor less than ten grams, and it should be clean and soft. If it is hard, it is an indication of the presence of copper, or possibly antimony, or other metals which may affect the cupellation. In such cases, and when the button is too large for the cupel, rescoring is necessary, and must be repeated until the button is brought to the condition fit for cupellation.

It is well to remember that the lead button will be brittle if there is very much silver or gold present, so that a brittle button is not always conclusive evidence that rescoring is needed.

In rescoring, a two-inch scorifier should be used for two reasons: 1. A larger scorifier is not necessary. 2. Where much work is being run the use of a two-inch scorifier for rescoring enables the assayer to keep better track of his work and permits him to rescore, at the same time he is pushing regular scorifications

with other samples. In rescorifying, lead may have to be added to complete the oxidation of the metals which render the lead button brittle, and care should always be exercised to keep the lead button up to near fifteen grams in weight.

The number of scorifiers that may be run at one time varies with the size of the muffle, its temperature, and the length to which it is heated uniformly and the character of the draft. It must be remembered that oxygen is as necessary as lead, or borax, to insure a good scorification. Where as many as three rows of scorifiers are run at one time, it will be found that lead buttons from the scorifiers in the last row will weigh from two to five grams more than those from the front row. This, in my judgment, marks the limit as to the number of rows of scorifiers. In some instances, with large muffles and strong drafts through the muffle I have been able to run five rows with less than five grams difference between the weights of the buttons produced by the last and front row of scorifiers.

It may happen that certain pulps spit during scorification. This may be due to too deep a scorifier in proportion to the charge; to dampness in the scorifier; to too low a heat; or to imperfect mixing of the pulp and lead, by which some of the pulp may rest on the bottom of the scorifier and evolve gases which throw off portions of the overlying melted lead. The assayer cannot always prevent spitting, but he must be on guard and, if it cannot be remedied otherwise, he may have to scorify certain pulps by themselves.

No scorifier should ever be used more than once, mainly for the reason that it is usually more or less attacked by the litharge, and if used a second time it is almost sure to be eaten through enough to leak.

In the event of the formation of a crust during scorification, do not resort to mechanical scorification by stirring with an iron rod, but add more lead, or some litharge or soda, and raise the heat; do anything almost except stir.

There are some ores that should be run colder than others, and a careful assayer will always determine by trial the best temperature for running any new ores. Such ores are not common, however.

It is a mistake to be sparing with the use of lead. Some ores require more than others to secure perfect decomposition of the ore. The tendency of assayers is to use too little lead and perhaps too much borax glass.

The following table gives an idea of the proper proportions, but they cannot be considered as exact figures, only guides:

	Weight of Ore.	Lead Gran.	Borax Glass.	Remarks.
Silicious ores.....	$\frac{1}{10}$ A.T.	45 gm.	$\frac{1}{2}$ gm.	High heat
Oxidized ores.....	"	50 "	2-4 "	Medium heat with add. of 1 gr. silica
Limey ores.....	"	60 "	4 "	High heat
Coppery ores.....	"	90 "	1.5 "	"
Zincy ores.....	"	60 "	4 "	"
Antimonial ores..	"	60 "	2 "	"
Sulphide ores.....	"	60 "	1.5 "	"
Chloride ores.....	"	45 "	1 "	Low heat
Telluride ores....	"	100 "	1 "	Litharge, 20 grams

The scorification method is generally used in the assay of silver ores. It should always be used for high grade silver ores. In Mexico, silver ores are usually contracted for by scorification assay, a requirement of the ore buyers, for the reason that the scorification assay is most apt to give results from one to four ounces lower than the same

ore gives by crucible assay. My own experience shows that increase of lead and scorification with larger volume of air will usually bring the results by the two methods very close together. Whatever error is made by the scorification method is always multiplied by ten, if one-tenth of an assay ton is used, while in crucible assay it is only multiplied by two.

### CUPELLATION

**123.** This is the operation of oxidizing, volatilizing, and absorbing the lead in the buttons derived from the scorification and crucible assays for gold and silver.

The operation is conducted in cupels made of bone ash which should be white, or grayish in color, and of about 80-mesh fineness. The dark bone ash implies imperfect burning with the possibility of evolution of gases in the operation of cupellation, which might cause spitting.

Different assayers have their own ideas as to the proper degree of fineness and hardness of the cupels, but from my own experience I cannot say there is any sensible difference in results due to small variations in the fineness and hardness of the cupels. I prefer to have my cupels of medium, but uniform, hardness, and make them in a cupel machine, as I believe cupels thus made are more uniform in degree of hardness.

The bone ash is thoroughly kneaded with the least amount of water (in which there is a little pearl ash dissolved), to make the bone ash moist, not wet. The cupels are made up in batches so that they will have at least one week to dry out in the air previous to using. Many assayers keep them for much longer periods; possibly they get better results by the more perfect dryness, but in the dry climate of the Southwest I have never

found any advantage in keeping them longer than one week.

There are certain patent cupels on the market which are recommended by their makers, giving the reason that the absorption loss is smaller with them than with the bone ash cupel. Such a recommendation counts against their use, as it would require a complete change in the prevailing methods of buying silver ores should they be adopted by the smelters and ore shippers. While the ore shipper wishes to secure the highest possible results in his assays, the "control" assayer cannot afford to secure high results by departures from the customary methods employed by assayers. If the "controls" are higher than smelter results, an "umpire" assay must follow, and the "umpire" assayer will adhere to the conventional methods.

I would only recommend these "patent cupels" to assayers who are traveling in the mountains and find it convenient to transport their outfit, including their cupels, from place to place. The "patent cupels" do not crumble so easily as "bone ash" cupels, consequently they are better adapted for transportation.

The cupels are made of convenient size from one inch to an inch and a quarter in diameter and from twenty to thirty grams in weight. A good cupel should absorb its own weight of litharge, but it is safer to have the cupels weigh forty to fifty per cent more than the weight of the lead button to be cupelled.

The cupels are placed in a row across the muffle and heated up to redness before the lead buttons are placed in them. This is done to insure dryness and burning out of all matter that might cause the evolution of gases and thereby contribute to "spitting." In doing first-class work there should be but one row of cupels in the muffle,

as the degree of heat can be more easily controlled. The muffle should have a strong current of air moving through it. The lead buttons are placed in order in the hot cupels, and the door closed for a few minutes, sufficient to allow the lead to melt and the small amounts of dross, which the buttons will always contain, to float off to the edges, leaving the lead button bright.

The muffle should then be opened and the cupels moved as near to the front as possible. The fumes of litharge should hang low, and the lead button should always be bright. Crystals of litharge should appear on the edges of the cupel, which is called "feathering"; but feathering may occur in a very strong draft, even when the lead buttons are too hot, and feathering may not occur when the temperature is right, owing to metallic impurities in the lead buttons. If the button "freezes" or becomes covered with litharge that cannot flow off, owing to the low heat, the losses of silver by absorption will be increased.

**124. Losses.** There are losses of silver in all cupellations, varying with the time taken in cupellation, the amount of silver in the button, the heat in the muffle, and the influence of metallic impurities in the lead button. The absorption loss is least at highest temperatures, when the loss by volatilization reaches its maximum. Experience alone, in the absence of facilities for accurately determining and regulating the actual conditions in the muffle as to temperature and amount of air introduced, is the only way of learning the proper manner of regulating the operation.

My own experiments show that the losses decrease with the decrease in the amount of lead to be burned off. From this I would recommend that the lead buttons be made very small before cupellation; but a certain amount of



lead is needed to collect all the silver in the pulp, in the operations of scorification and crucible assay. The minimum size of the lead button, generally speaking, is fifteen grams, consequently I cupel buttons weighing not less than fifteen nor more than twenty grams.

It frequently happens that it is necessary to make the lead buttons larger than twenty grams. In such cases they should be rescorified till they attain the proper weight before cupellation.

The following table gives the losses in silver from cupellation alone, with no impurities, except lead:

Ozs. Per Ton.	Temperature of Cupellation.		
	760°-820°	960°-1020°	1200°-1250°
10	2.58%	5.37%	7.84%
42	1.60	2.34	3.81
100	2.16	4.16	4.07
200	2.51	2.55	3.90
400	1.91	2.46	3.05
750	1.79	2.64	3.09
1500	1.41	2.58	3.09
3000	1.12	2.28	2.51
5500	0.93	1.45	2.02
10000	0.67	1.07	1.64

Similar experiments with gold showed no loss whatever when the cupellation was conducted at about 1000° C. At a temperature of 1500° C. the loss of gold was from two-tenths to one per cent.

Other experiments showed that the presence of gold diminished slightly the losses of silver; also that increasing the size of the lead button, thereby increasing the time of cupellation, increased the losses of silver up to ores of 1500 ounces to the ton; with ores richer than 1500 ounces there was but little difference so long as

the lead buttons did not weigh more than twenty-four grams.

The experiments made by Lodge \* confirm the results obtained by me.

In cupellation, after the lead has been removed, the cupel should be pushed back in the hotter part of the muffle to drive off the last traces of lead, some of which is likely to be retained, if this is not done, by a large silver button.

The "blicking," which occurs with large buttons, is not looked for ordinarily.

If the silver button is large, it should be covered with a hot cupel before withdrawing it from the muffle, otherwise it is apt to "sprout" by the absorption of oxygen just at the close, which is expelled by the contraction of the button on cooling, sometimes with enough violence to propel particles of the silver for considerable distances, causing losses of silver and gold.

In cupellation, according to experiments of Prof. C. H. Fulton, the temperature for uncovering is between 800 and 840° C.; the temperature of cupellation is about 850° and usually rises above that temperature, unless the muffle temperature is lowered to 930 and 940° C.; the temperature of finishing should be above 850° C. The temperature of the muffle walls is quite different from the temperature of the muffle close to the cupels. Professor Fulton also emphasizes the necessity of regulating the air drafts of the muffle as well as its temperature.

\* Notes on Assaying, Lodge, pp. 61, 62, 63.

## PARTING AND WEIGHING

125. The silver button with whatever gold was in the ores is weighed. If a half assay ton of pulp is used, the troy ounces per ton of 2000 lbs. avoirdupois is equal to the weight of the silver button in milligrams multiplied by two. If one-tenth of an assay ton is used, the weight of the silver button in milligrams is multiplied by ten. From these results the amount of gold found is deducted.

If the metric system is used, 10 grams of pulp are used for each crucible assay, and 2 grams of pulp for each scorification assay. In the metric system the silver is usually reported in kilos per metric ton. When 10 grams of ore are used, the weight of the bead in milligrams multiplied by 100 is the number of grams of silver per metric ton. If 2 grams are used, multiply by 500. Gold is always reported in grams per metric ton.

In weighing pulps for fire assays, the balance should be sensitive to one-tenth of a milligram, in which case the error from weighing the pulp will only be in scorification assays plus or minus 0.005 per cent.

The silver buttons should be weighed on a balance where the sensibility is at least  $\frac{1}{10}$  of a milligram, making the error in weighing plus or minus 0.002 per cent if the silver button found weighs but 1 milligram. If this is multiplied by 500, as is necessary when 2 grams of pulp are used, the possible error is also multiplied, making the possible error plus or minus one per cent. If one-tenth of an assay ton is used the error is only multiplied by 10, making it plus or minus 0.02 per cent.

The silver buttons are then thrown into porcelain crucibles of small size and perfectly clean, and covered with a few cc. of water; nitric acid, concentrated, is then added,

drop by drop, until it begins to bite the silver. Solution is hastened by gentle heat. The silver dissolves readily if there is some gold in the bead, unless the amount of gold is large, equal to one-fourth of silver. If the silver is free from gold, the acid does not act readily, but by heating, and not allowing the acid to become too strong, the silver is finally all dissolved. It may be necessary to alloy silver with the button, so there will be at least four parts of silver to each part of gold; silver foil is used for this purpose, and, if the muffle is hot, it is best to put the silver foil and button into a cupel with three or four grams of lead and cupel the button. In this way there is less danger of losing the silver button. If the muffle has cooled down, the button is wrapped in the silver foil and the mass is fused on a piece of charcoal with the blowpipe. It must be thoroughly fused so the alloy will be of uniform composition. It is then treated with nitric acid in the porcelain cup until all the silver is dissolved. After all the silver is dissolved and there are no dark specks remaining, it is certain there is no gold in the sample. Any black or brownish matter may be gold, or various insoluble impurities, but when these are found the work must proceed the same as if they were gold.

After the silver is dissolved, the liquor is decanted off; and if the brown residue is considerable, it should be again treated with a mixture of equal parts of strong nitric acid and water, heating the crucible. The solution is then poured off and the crucible filled with pure water; this is then decanted and the operation repeated. Then cover with dilute ammonia (1:4) to dissolve any silver chloride that may have been formed by impurities in the water; after the washing with ammonia, wash again with pure water. At this last washing, before decantation, be careful to unite the residue in one mass by judicious

tapping of the crucible, and keep it together in the crucible while making the decantation. Then dry the crucible with gentle heat and heat it to dull redness in the muffle, or with any convenient source of heat. After cooling, brush the gold out of the crucible on to the scale pan of a button balance, whose sensibility is  $\frac{1}{800}$  of a milligram, and weigh. The value of the ore is determined as in calculating the value of silver.

In assaying for gold at least half an assay ton of the pulp should always be used.

The operation of determining the amount of gold in an ore by fire methods, is one of the most accurate of analytical methods. The principal source of error is due to the instrumental error of the balances, except in some special instances. With a balance weighing to the five-hundredth part of a milligram, and using one assay ton of ore, it is possible to report the gold to one five-thousandth part of an ounce, which is within 0.000017 of one per cent of the contents of the ore.

**126. Valuation of Ores.** The smelters always pay for all the gold in the ores when there is one-tenth of an ounce to the ton. If less than one-tenth no pay is given, except by special contract. The average price paid is \$19.50 per ounce.

Silver is always paid for when there is an ounce or more to the ton, at the rate of 95 per cent of the New York quotation on the day of sampling. The smelter, of course, makes charges for smelting, varying with the composition of the ores as determined by analysis.

## SILVER BY WET ASSAY

**127.** The oldest volumetric method for the determination of silver is that of Gay-Lussac, in which precipitation is made with a standard solution of sodium chloride, but it seems to me that the following method, except in the presence of large amounts of copper, is far more satisfactory.

**128. Volhard's Method.** A definite amount of the substance, from one-half to ten grams, is treated with nitric acid to decomposition and solution of the silver salts. If bullion is to be tested, use nitric acid of about one part of acid to three parts of water. If pulps are to be tested, start with concentrated acid, and after decomposition is effected, dilute with distilled water and filter. Collect the filtrate in a beaker of 400 cc. capacity.

**129. Titration.** Add half a gram of ferric sulphate to the beaker, and when dissolved run into the cold liquid a standardized solution of ammonium sulphocyanate. To make a solution of which 1 cc. will be equal to 0.005 gram of silver, dissolve about 4 grams of the pure crystallized ammonium sulphocyanate in a liter of distilled water. The salt varies somewhat in the amount of water of crystallization, and it is perhaps best to dissolve the salt in 900 cc. of water and determine its strength in silver, and then add enough more water, learned by calculation, to make the desired strength. The ammonium sulphocyanate is run in to first permanent pink coloration. Owing to the curdy nature of the precipitate, it must be thoroughly stirred in titrating to break up the clots which may entangle some of the liquid. As the burette will only read to one-tenth of a cc., it is desirable to run down to near the end reaction with the normal solution, and finish with a solution one-tenth the strength.

The sulphocyanate solution is standardized against pure silver foil.

I have used this method in an emergency as a substitute for a fine button balance with good results. The silver button obtained by the usual fire methods was dissolved of nitric acid, and titrated with a sulphocyanate solution of which one cc. equalled a milligram of silver. If one-tenth of an assay ton of ore is taken, it is necessary to multiply the cc. used by ten to find the troy ounces of silver per ton of 2000 lbs.

#### GOLD BY WET ASSAY

130. It may be necessary at times to make such a determination. A suitable quantity, from ten to one thousand grams, of the finely powdered mineral is placed of a large bottle, thoroughly wetted with water, and then treated with 500 cc. of bromine water for a period of several days. The bromine dissolves the gold as bromide with portions of other metals. The solution is filtered off, the residue washed thoroughly, and sodium peroxide added to the solution, precipitating metallic hydroxides together with the gold, according to the equation:



The precipitated hydroxides are then taken up with hydrochloric acid, and after the gold has settled, decant off as much of the liquid as possible, finally bringing the gold on a small filter, after which it is dried, ignited, and weighed as metallic gold.

## BULLION

**131.** The purity of bullion is expressed in parts per one thousand. The following classes of bullion are known in the trade:

“Gold bullion,” when 50 per cent of the weight is gold;

“Doré bullion” contains 900 parts of silver with some gold and some base metals, as copper, lead, antimony, etc.;

“Fine silver,” running 990 to 999 fine with no gold, and pure enough to use in the arts and for coinage.

“Base bullion” contains a very large amount of base alloys and from 100 to 900 parts of silver, with or without gold.

**132. Sampling.** In assay offices the samples of bullion are usually made by drilling small holes in the bars one-fourth of an inch in diameter to a depth of one-half to two inches, as may be convenient. Two holes should be drilled, one on one face towards the end and the other on the opposite face and end. Where much bullion is handled, as in the mints, the sampling is more carefully done according to standard rules.

**133. Assay.** Weigh off three portions of the sample of about 10 grams each and place each in a scorifier with 40 to 50 grams of test lead, scorify, and then cupel.

At the time of cupellation, check cupellations of silver should be made by weighing off portions of pure silver, equal, or nearly equal, to the weight of the silver in the bullion; wrap this silver up in fifteen grams of lead foil, and place the cupels alternating with the cupels containing the bullion. Begin cupellation at same time, and carefully cupel with feathering, being careful to move the cupels back to the hotter part of the muffle to finish, so as to drive off the last portions of lead.



The loss of silver found in the check assays is averaged and added to the weight of the silver found in the bullion. If the bullion contains copper, it is advisable to add an equivalent amount of copper to the check assay.

If the bullion will cupel directly, the scorification is omitted, and as the loss of silver increases with the time of cupellation no more lead is added than is necessary. After the silver buttons are weighed, the gold is determined by parting.

**134. Assaying Copper Mattes.** In the removal of copper by rescorifications in mattes and pulps containing large amounts of copper, the losses of gold and silver are often as high as four and five per cent. The following method is generally used now for such samples:

One-half assay ton of the pulp is placed in a 500-cc. beaker, 100 cc. of distilled water are added, and the whole mass thoroughly stirred; then add 50 cc. of concentrated nitric acid and allow to stand for half an hour at room temperature; then add 50 cc. more, and warm the solution until all action ceases and all brown fumes are driven off. The beaker is then filled up with water and stirred, after which it is allowed to settle, and then filtered, catching the filtrate in a liter flask. The dried residue is then assayed for gold by the fire method in a crucible. A solution of sodium bromide is then added in slight excess, being careful not to add much excess. Ten cc. of a saturated solution of lead acetate are then added and the solution stirred, followed by the addition of 2 cc. of sulphuric acid to facilitate settling. As soon as the filtrate has settled, filter off, wash and dry in a scorifier, together with the insoluble residue from the first filtration, burn off the paper, add 50 grams. of test lead, 5 grams of litharge and half a gram of borax glass, and scorify. The lead buttons are cupelled in the usual way.

**135. Assay of Silver Precipitates.** Owing to their high content of silver, the loss in the usual method is too high to be ignored, and it is customary to assay such material by what is called "corrected assay." Ten scorifiers are run with one-tenth of an assay ton of the pulp with sixty grams of test lead and three grams of borax glass.

The slags which are broken off from the lead buttons made in the scorification are saved.

The lead buttons are cupelled separately and the cupels are added to the slags. The slags and cupels are then crushed and mixed with 50 grams of lith rge, 30 grams of borax glass, 50 grams of soda ash, and  $2\frac{1}{2}$  grams of argols, placed in a crucible, and assayed. The silver found is added to the average amount of silver found in the first assays.

## CHAPTER XI

### IRON

**136. Ores.** Magnetite, red and brown hematite, limonite, and siderite, are the most important minerals forming ores of iron. Iron pyrites are abundant and widely distributed, but are not suited for the direct manufacture of the metal; large quantities of pyrites are roasted to make sulphuric acid, and most of the residual iron oxide finds its way into the iron furnaces.

**137. Detection.** Dissolve a small portion of the powdered mineral in a small amount of hydrochloric acid to which a few drops of nitric acid have been added, then make alkaline with ammonia water, when a reddish brown precipitate will indicate the presence of iron. If a delicate test is needed do not use the ammonia water, but add a drop of potassium sulphocyanide, when a deep red coloration is produced.

**138. Methods.** The volumetric methods employed for the determination of iron are all accurate, satisfactory and convenient, so far as the titrations are concerned. In western practice the total iron is seldom asked for, only that which will be taken up by the conventional acid treatment. While there are certain precautions to be observed in the determination of iron, notably the reduction from ferric to ferrous condition, the differences in results are most likely due to the differences in the effects of the acids in decomposing the ores under varying conditions.

**139. Decomposition.** One-half gram of ore is placed in a casserole or flask, to which 10 cc. of concentrated hydrochloric acid are added, and warmed gently so long as decomposition is apparent. If sulphides are present, 5 cc. of nitric acid must be added to secure their decomposition, but on account of its interference in the subsequent reduction of the iron, if not removed, it is well to avoid the use of nitric acid, if that is possible. Now add 5 cc. of sulphuric acid and boil off all free acid, cool, and add water, boiling to ensure complete solution.

In the event that hydrochloric acid alone will accomplish apparently perfect decomposition, the treatment with nitric acid and sulphuric acid may be omitted. The residue should be white, or colorless.

**140. Reduction.** There should be no nitric acid in the solution, but only hydrochloric or sulphuric acid. Zinc is generally employed to accomplish the reduction, particularly when sulphuric acid is present. I have found aluminum more rapid than zinc, and as it may be readily secured now free enough from iron, I employ sheet aluminum for the reduction of the iron in the bichromate as well as in the permanganate method. The reduction with aluminum is more rapid than with zinc, and if the iron is in a hydrochloric acid solution the reducing action of aluminum is as rapid as stannous chloride.

The reduction is accomplished in a flask of about 200 cc. capacity by bringing the solution to a boil and keeping it in that condition until the solution becomes colorless. So soon as reduction is complete, fill the flask with water up to the neck and allow it to stand until cool. Sheet aluminum, such as is used for copper, is used.

When zinc is used to reduce iron solutions it is employed in the form of sticks, sheets, shot or powder.

When stannous chloride is used to reduce the iron, a

hydrochloric acid solution is necessary. It is heated to boiling and the stannous chloride added cautiously, drop by drop, and towards the last allowing the interval between each addition to lengthen, so as to avoid any considerable excess of stannous chloride. The solution is kept warm until ready to titrate; and just before titration add ten cc. of a saturated solution of mercuric chloride to take up any excess of stannous chloride. Should the solution become blackish it shows that the excess of stannous chloride was very large, and it is best to throw away the assay and start anew. The solution should become grayish, and if it does not it is probable that all of the iron was not reduced, spoiling the value of the determination. As it is impossible to use an excess of aluminum, I prefer it to the stannous chloride.

The reactions involved in reductions are shown in the following equations:

With zinc:  $\text{Fe}_2(\text{SO}_4)_3 + \text{Zn} = \text{ZnSO}_4 + 2\text{FeSO}_4$ .

With aluminum:  $\text{Al}_2 + 3\text{Fe}_2\text{Cl}_6 = \text{Al}_2\text{Cl}_6 + 6\text{FeCl}_2$ .

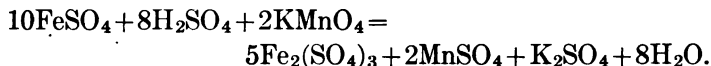
With stannous chloride:  $\text{Fe}_2\text{Cl}_6 + \text{SnCl}_2 = 2\text{FeCl}_2 + \text{SnCl}_4$ .

When zinc or aluminum is used for reduction, small amounts of hydrogen gas remain in the liquors, unless the excess aluminum or zinc is removed while the solution is boiling hot. The hydrogen consumes permanganate, giving a higher result than the true iron content.

**141. Titration with Permanganate.** When ready for titration, decant the solution of ferrous salt into a beaker of about 700 cc. capacity and run in a standardized solution of potassium permanganate until a faint permanent pink color is reached. Then wash out the flask into the beaker with tap water free from iron, and carefully run to end reaction. The volume of the solution should

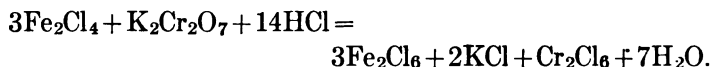
be about 600 cc., and it should be cooled to room temperature before titration.

The reaction is:



**142. Standardizing Permanganate.** Dissolve 2.83 grams of potassium permanganate in a liter of distilled water to make a solution of which 1 cc. will equal 0.005 gram of iron. Standardize against a solution made by dissolving 1 gram of pure ferrous ammonium sulphate in a previously cooled mixture of 700 cc. of water acidified with 5 cc. of sulphuric acid or an equal amount of hydrochloric acid, according to which acid is generally used to decompose the ores. Run in permanganate to a faint permanent pink color. The ferrous alum contains 14.25 per cent of iron, consequently the strength of the permanganate is found by dividing 0.1425 gram by the cc. of permanganate used.

**143. Titration with Potassium Dichromate.** The reaction in this method is as follows:



The iron must be in the form of a hydrochloric acid solution of ferric chloride, obtained as described in section 139. The bulk of the solution should not be less than 50 or more than 125 cc. The reduction with aluminum in complex ores is particularly desirable, as it leaves an iron solution with fewer interfering constituents. The solution of dichromate is run in from a burette, while stirring the iron solution. The end reaction is determined

by using a dilute solution of potassium ferricyanide on a porcelain plate. So long as there is ferrous chloride in the solution, a drop of it will give an intensely blue color with the ferricyanide. When the coloration becomes faint, proceed cautiously, drop by drop, and use less and less of the ferricyanide solution, to increase the delicacy of the end reaction. Should this precaution pass unheeded, an abnormal color is likely to be produced which will obscure the end-point. The number of cc. used multiplied by its strength in iron gives the weight of iron, from which the percentage may be calculated.

**144. Standardizing Dichromate Solution.** Four and four-tenths grams of potassium dichromate dissolved in a liter of water will give a solution of which one cc. will approximate 0.005 gram of iron.

The indicator solution of potassium ferricyanide is not permanent, and should be freshly prepared. One-tenth of a gram of it in fifteen cc. of water is the best strength.

If the analyst cares to use stannous chloride as the reducing agent, he had best prepare it from pure tin by dissolving fifteen grams in strong hydrochloric acid, and when solution is accomplished, adding 300 cc. of concentrated hydrochloric acid and diluting to a liter.

Standardize by weighing off 0.15–0.2 gram of pure iron wire, supplied by dealers for this purpose, and dissolving it in a 200-cc. flask in five cc. concentrated hydrochloric acid and twenty cc. of water.

Warm gently, and when the wire is nearly dissolved, add one-tenth of a gram of potassium chlorate, in small crystals, to destroy all hydrocarbons present.

When solution of the iron is completed, add five cc. of concentrated hydrochloric acid and boil for a few minutes to decompose any undecomposed potassium chlorate.

Reduce with zinc, aluminum, or stannous chloride,

according to the method of reduction employed in testing the ores, and run in the dichromate as described in 139.

In standardizing with iron it is well to remember that the best iron wire is usually only 99.8 per cent pure, and many chemists will make corrections for this. It is not a necessary precaution, however, in all classes of technical work, and it is probable that errors due to manipulation may be greater than that due to the impurities in the iron.

**145. Mercuric Chloride Solution.** There should be kept on hand a saturated solution of mercuric chloride in water (about sixty-five grams to the liter). If it is necessary to make up this solution quickly, put the mercuric chloride in a porcelain mortar, moisten it with two or three drops of alcohol, and rub it with the pestle as the water is gradually added. Otherwise it requires several days for the water to become saturated with the salt.

**146. Organic Matter.** In ores containing organic matter, the weighed sample should be ignited in a porcelain or platinum crucible previous to acid treatment.

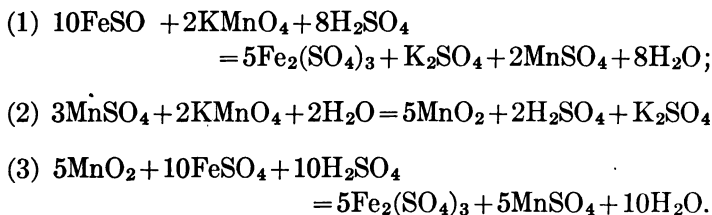
When titanium is present, a special method must be used, which will be found in Vol. I, "Fresenius, Quantitative Analysis," p. 111.

**147. Effect of Air.** Hot solutions of ferrous salts absorb oxygen from the air with sufficient rapidity to sensibly alter the results. It is therefore best to perform the reduction in flasks, and immediately after removing the reducing agent fill the flask up to the neck with boiled water; on cooling to room temperature the oxidation is small owing to the limited area in contact with the air.

**148. Effects of Varying Bulk.** There is very little effect from varying the bulk, provided the variations do not exceed more than 200 cc.



**149. Effect of Varying Acids.** In the permanganate method the amount of hydrochloric acid present must be kept at a minimum amount of not more than five cc. excess, and should never exceed that. Sulphuric acid is best for permanganate titration, the results not being affected unless the acid drops below five cc., when there is danger of the permanganate reacting with the manganese, causing a brown coloration. If this happens, add five cc. sulphuric acid and stir thoroughly. If the precipitate does not immediately dissolve, add a weighed portion of ferrous ammonium sulphate and stir; 0.1 gram of the ferrous ammonium sulphate should be enough. The precipitate should dissolve at once, and the solution become clear. The titration can now be continued, the true iron content being obtained by deducting from the final result the iron content of the ferrous ammonium sulphate, as will be seen from the following reactions:



In the dichromate method variable quantities of hydrochloric acid produce no effect.

**150. Effect of Foreign Salts.** In the permanganate method there are no salts that would naturally be present which would alter the results. The same remark applies to the dichromate method. It is well, however, to remember that if large quantities of lead, or bismuth, are present in the solution they might, under certain conditions, show a large consumption of dichromate.

Zinc cannot be used to reduce iron when the dichromate is used, for it decreases the consumption of dichromate.

**151. Valuation.** Iron ores vary in value from three to seven dollars per ton, when employed for the manufacture of iron. The amounts of sulphur, phosphorus, and titanium present largely diminish the value of the ore, which also varies with the percentage of iron.

In the lead smelters the iron in the ores bought is usually paid for at the rate of from five to ten cents per unit.

## CHAPTER XII

### LEAD

**152. Ores.** Galena, the sulphide, and cerussite, the carbonate, are the most abundant of the lead minerals; next in importance is anglesite, the sulphate, while the other minerals containing lead as a constituent are interesting, but of little importance as ore supplies.

**153. Detection.** Heated with sodium carbonate on charcoal with a reducing flame, the compounds of lead are reduced easily to the metallic state, and small globules of metallic lead will float in the mass. By the judicious use of the oxidizing flame, the presence of lead may be verified by the production of the lemon-yellow coating of the oxide.

The best wet test is to treat the substance with a small amount of nitric acid to decompose it, add a few cc. of water to the solution, and then add a drop or two of a solution of potassium iodide; a deep orange precipitate of lead iodide is formed. Small amounts of lead may be detected in this way, provided the solution is clear and is cooled to room temperature before adding the iodide.

**154. Methods.** The technical estimation of lead is of great importance. The oldest method is the fire method, now falling into general disfavor. Assayers running on an ore which varies but little in character, become accustomed to the exact conditions for the particular ore, and are able to make accurate determinations by the fire method. When the ores are constantly varying, the results are positively unreliable. Pulps weighed

in duplicate, with the same flux, in composition and quantity, placed in the muffle side by side and remaining for the same period of time, will often give results showing differences of as much as five per cent, while the same pulp with no change in the flux, but conducting the assay at a higher or lower temperature, or by varying the time of heating, will, at other times, give good checks. There are so many factors of variation in the fire assay for lead that a careful assayer, when given a new pulp, will always make a wet determination, by which he learns the true percentage of lead in the ore, and can then learn the conditions of the fire assay, so that after trial he can secure as reliable results by fire assay as he can by the wet methods. With many ores it is possible to run the fire assay so that the amount of lead found will be greater than the actual amount of lead in the ore. In other words, enough of zinc, arsenic, and other metallic impurities in the ore are thrown down in the lead button to more than offset the lead lost by volatilization and in the slags. The lead button will frequently, under these circumstances, still stand the test of malleability by being beaten out into a sheet. As a rule, a fire assay gives a lower result than that obtained by the wet method, but I have never yet encountered an ore in which I could not, by repeated trials, so modify the conditions for the fire assay as to secure results that would check with those by the wet method.

The wet method best known and most generally employed is known as Alexander's molybdate method. The original method is not reliable on low-grade ores which carry much lime, and it frequently fails when there is iron in the ores; all of the iron sulphate failing to go into the solution, at the time of the filtering off the lead sulphate, it goes along and obscures the end reactions

with the solution of tannic acid; sometimes the obscuration is so great that the determination is worthless. To overcome these objections Mr. A. H. Low has modified the method, adding to its length but making it a perfect volumetric method.

The chromate method herein described has been developed in my laboratory, and has been tried out thoroughly on all varieties of ore, in connection with all the other known methods, and has proved itself to be the equal, if not the superior, of them all.

It is customary for the smelters to deduct two per cent from the results obtained by a wet determination in settling for ores, it being assumed that a fire determination will always be lower than a wet. While I do not agree with this assumption, it is decidedly better for both parties to accept this arbitrary deduction and settle for lead only by wet determination.

**155. Author's Chromate Method.** Weigh out half a gram of the pulp into a No. 1 casserole, cover the pulp with from five to seven cc. of concentrated nitric acid, and set the casserole in a warm place where the temperature will not exceed 40° C., and keep it there for at least ten minutes; then add five cc. of concentrated hydrochloric acid and allow it to stand for at least another ten minutes. The casserole is kept covered with a watch-glass during the entire operation. Put the casserole on a hot plate and evaporate to dryness at a gentle heat; avoid spattering as far as it is possible, then cover with from five to ten cc. of sulphuric acid, and heat until the sulphuric fumes come off strongly. Then remove from hot plate, and when it is cooled slightly, add water from a jet to the amount of about fifty cc. Rinse the watch-glass off into the casserole and allow it to stand for a few minutes. The lead sulphate settles quickly, and the over-

lying liquor is decanted through a 7-cm. or 9-cm. filter, S. & S. No. 589; the lead sulphate is washed twice by decantation, so as to keep the lead sulphate in the casserole as far as possible. It is only necessary to wash out any soluble salts of bismuth, mercury, and silver that may be present, as well as all free acid. I have usually found two washings, each with fifty cc. of pure water, entirely sufficient.

**156. Solution of Lead Sulphates.** Add about five grams, by measure, of crystallized sodium acetate to the casserole, then ten cc. of water and two or three drops of dilute acetic acid, put the casserole on the hot plate, and heat to boiling. All of the lead sulphate will quickly dissolve, as the analyst will learn to discern. A clean beaker, not to exceed 125 cc. in capacity, is placed beneath the funnel through which the decantation was effected, and the hot solution from the casserole is poured over the filter. About twenty cc. of water are then put in the casserole, and if there is any undissolved lead sulphate, add one or two grams of sodium acetate, heat the water to boiling, and pour over the filter; repeat this operation twice, and wash the filter paper once with cold water. The bulk of the filtrate should not exceed fifty cc. on low and medium grade ores, unless it should be found absolutely necessary in order to dissolve all of the lead sulphate, which I have never had occur even with a pure galena. By keeping the bulk down to fifty cc., I have obtained the characteristic yellow precipitate of lead chromate on the addition of the potassium chromate, when there was only 0.05 of one per cent of lead in the pulp. The filtrate is kept hot until ready to be titrated.

**157. Titration.** The standard solution is made by dissolving 4.9 grams of potassium chromate in a liter of distilled water. The indicator solution is made by

dissolving one-tenth of a gram of silver nitrate in one hundred cc. of distilled water. In titrating, drops of the indicator solution are placed on the spot plate with a stirring rod. The titration is accomplished by setting aside about half of the solution and running in the standard solution of chromate from a burette, until a strong end reaction is obtained with the silver nitrate, the silver nitrate showing red silver chromate when the chromate is in excess. Then add part of the reserved portion, running down to end reaction, repeating this, finally rinsing out the reserved beaker until, after allowing the lead chromate to settle for a moment, a drop of the liquid gives a faint purplish coloration with the silver nitrate. From the burette reading deduct one-half a cc. for each fifty cc. in excess of fifty measured by the filtrate.

The chromate solution is standardized by dissolving one gram of pure lead sulphate by boiling it with forty grams of sodium acetate, twenty cc. of pure water, and two drops of dilute acetic acid. When thoroughly dissolved, dilute to 250 cc. and take fifty cc. for a titration, which is made as before described. 0.13658 divided by the cc. of standard solution used will give the strength of one cc. in metallic lead. Prepared as directed, one cc. will equal 0.005 gram of lead.

**158. Remarks.** It is very important that the strength of the indicator be kept weak, just enough to show the color of silver chromate. If a strong solution is used for the indicator, it will be found that the silver nitrate will take away chromic acid from the suspended lead chromate, thereby giving an end reaction before all of the lead has been precipitated. It is also important that the solution should be nearly neutral to make the end reaction as sensitive as necessary. A very slight excess of acetic

acid is less harmful than a little excess of alkali. By remembering these two points, the analyst will never have any difficulty, and if his results do not check within one-tenth of one cc. he can rest assured that he has been careless, or some unobserved mishap has occurred. This method was first published in the April, 1908, number of the *Journal of the Western Chemist and Metallurgist*, where more information may be found.

The method as outlined here is modified somewhat from the original description, the result of greater experience. On ores running fifty per cent of lead and over, I would advise taking only about 0.3 of a gram of the pulp, for the method works best when the bulk of the liquid at the commencement of the titration is not more than fifty cc.

**159. Molybdate Method, Low's Modification.** Weigh half a gram of ore into a 200-cc. flask. If a mixed sulphide, treat with about ten cc. of strong nitric acid, boiling gently until the decomposition is complete. If partly, or wholly, an oxidized product, the nitric acid may fail to effect a good decomposition, and it is better to begin with ten cc. of strong hydrochloric acid and heat gently until all the iron oxide, etc., is in solution, then, if necessary, add five or ten cc. of nitric acid and heat again to decompose sulphides. A pure or nearly pure galena is also best attacked with hydrochloric acid. Take ten cc. of strong acid and twenty cc. of water and boil gently until the decomposition is as complete as possible and the hydrogen sulphide all expelled. If sulphides that resist hydrochloric acid still remain, add a little nitric acid and continue the heating.

Decomposition having been satisfactorily effected, add seven cc. of strong sulphuric acid and boil, best over a free flame, until the white fumes are coming off copiously. Cool, add about twenty-five cc. of water, and heat to



boiling. Allow to stand, hot, for a short time until the anhydrous iron sulphate usually present has dissolved, and then cool to room temperature and filter. Wash well with cold dilute (1:10) sulphuric acid. Retaining the filter in the funnel, rinse the residue from it as completely as possible, with cold water, back into the flask. Add five grams or more of crystallized sodium acetate and about 1 cc. of strong acetic acid, together with a little more water if apparently necessary. Heat to boiling, and see that the lead sulphate is entirely dissolved, adding more of the solvents if necessary. Now filter through the last filter, and wash well with hot water, receiving the filtrate in the original flask. Instead of proceeding as thus described to effect the solution of the lead sulphate, it will usually suffice to dissolve it directly on the filter with a boiling-hot solution of sodium acetate. Prepare the latter by making a cold saturated solution of the commercial salt and adding to each liter 40 cc. of 80 per cent glacial acetic acid. Heat to boiling in a wash-bottle for use. It dissolves the lead sulphate on the filter very easily. Now add an excess of ammonium sulphide solution and boil for a moment to coagulate the precipitated lead sulphide. Allow to settle a short time, and then filter and wash with hot water while hot. By these operations any calcium sulphate is practically all removed and passes into the filtrate.

The lead sulphide is still liable to contain a little iron, especially if the ore is high grade. This iron is originally retained by the lead sulphate. If allowed to remain, it tends to obscure the end-point of the subsequent titration by producing a color with the tannic acid used for testing. It is best, therefore, to remove any possible iron in every case as follows: Pour through the precipitate on the filter a mixture of 5 cc. of the dilute (1:10)

sulphuric acid and 15 cc. strong hydrogen sulphide water, and then wash with cold water. Now drop filter and contents into the flask, and add five cc. of strong hydrochloric acid. Boil the mixture to convert the lead to chloride and expel hydrogen sulphide, the filter meanwhile becoming well disintegrated. If five cc. of hydrochloric acid prove insufficient to entirely decompose the lead sulphide, add a little more, but avoid using a large excess. To oxidize any unexpelled hydrogen sulphide, add a few drops of strong nitric acid to the hot mixture. Now add twenty-five cc. of cold water and a few drops of litmus solution as indicator, and add strong ammonia cautiously, avoiding much excess, until the litmus paper turns blue. Now make distinctly acid with strong acetic acid. Heat the mixture in the flask to boiling, dilute to about two hundred cc. with boiling water, and titrate with the standard ammonium molybdate solution as follows:

Pour about two-thirds of the hot lead solution into a large beaker and run the molybdate solution into it from a burette until a drop from the beaker, when placed on a glazed porcelain plate and touched with a drop of solution of tannic acid (about one-tenth of a gram dissolved in twenty cc. of water), gives a brown or yellow tinge. Now add more of the lead solution from the flask and continue the titration until the end-point is again passed. Continue to thus approach the true end-point, using more caution each time. Finally, when only a few cc. remain in the flask, pour the entire mixture in the beaker into the flask and then back into the beaker again and finish the titration two drops at a time. When the final yellow tinge is obtained some of the immediately preceding tests may have developed a tinge also. From the reading of the burette deduct the volume of two drops for each test,

thus showing color. Multiply the corrected reading by the percentage value of one cc. of the molybdate solution in lead to obtain the percentage of lead in the ores.

**160. Standardizing the Molybdate Solution.** Dissolve 4.74 grams of ammonium molybdate in a liter of water to make a solution of which one cc. will correspond to one per cent of lead when half a gram of ore is taken. Standardize by weighing out two-tenths of a gram of pure lead sulphate into a beaker of 300 cc. capacity, and dissolve by warming with a mixture of 2 cc. strong nitric acid and 4 cc. water. When dissolved, boil nearly or quite to dryness, add about 50 cc. of water, and see that all the lead nitrate dissolves. Now add 5 cc. of strong sulphuric acid, boil the mixture a moment, cool to room temperature, and allow to stand and settle for a short time. Filter and wash with dilute (1:10) sulphuric acid. Proceed with the filter lead sulphate as in 159, except that the purification of the lead sulphide may be omitted. 0.13658 divided by the cc. of molybdate used will give the strength of one cc. in metallic lead.

**161. Alexander's Method.** A half gram of the pulp is taken and decomposed in a casserole, or beaker, or flask, as the analyst may prefer, with nitric and hydrochloric acids. After the decomposition, add ten cc. of concentrated sulphuric acid and boil until the fumes come off copiously; then cool, add twenty-five cc. of water and filter off the lead sulphate, washing with dilute sulphuric acid. The filter and precipitate are then placed in a beaker of 300 cc. capacity, ten cc. of concentrated hydrochloric acid added, and boiled until filter is disintegrated. Then add fifteen cc. more of strong hydrochloric acid, twenty-five cc. of water and twenty-five cc. of strong ammonia water, and boil until the lead sulphate is completely dissolved. Make alkaline with ammonia water, and then

acid with strong acetic acid, and titrate as previously described, 159.

The defects of this short method have been previously noted in this chapter. The method is given because it is the form of the molybdate generally employed. It will give good results when the ores carry little lime and iron, and when the lead content is not too high or too low; but the method is not at all suited for work where the ores come from many sources and are liable to have all sorts of constituents.

**162. Molybdate Method Used by the Author.** The author avoids the difficulties from lime and iron in the molybdate method by following this treatment: One-half a gram of the ore is weighed into a No. 2 casserole and treated as in 155. The washed lead sulphate is then washed from its filter into the original casserole, five grams of ammonium chloride and two cc. of hydrochloric acid are added, and the bulk made up with water to about 60 cc. and boiled until the lead sulphate is in solution. A V-shaped piece of aluminum is then placed in the casserole and boiled for about five minutes, when the lead will be completely precipitated. The lead is collected into one mass by shaking, and the aluminum removed and set aside. The liquor is decanted off from the lead, which is then washed with cold water two or three times. The lead is then dissolved in as little strong nitric acid as necessary, treating the aluminum with the same acid to dissolve any adhering lead, and mixing the washings from it with the solution of lead nitrate in a 300-cc. beaker. The solution is then made alkaline with ammonia water, and then acid with strong acetic acid, and heated to boiling temperature, when it is titrated with the ammonium molybdate, as described in 159.

This modification gives satisfactory results, but I

consider the chromate method far more certain and accurate, particularly so for low-grade ferruginous ores.

**163. The Electrolytic Assay of Lead (Guess-Haultain Method).** The anode is 12.5 cm. long, and is divided into a blade 4 cm. wide and 6.25 cm. long, and a tongue 0.7 cm. wide and 6.25 long, the immersion area being 50 sq.cm. The blade is first sand-blasted, and then corrugated lengthwise, in order to impart the necessary rigidity. Strips of platinum foil 12.5 cm. long, and 0.5 cm. wide, having a medium corrugation, form the cathode. Three electrodes are used in each cell; one anode in the middle and one cathode on each side of the anode. The electrodes are connected with slotted aluminum terminals, in which they are held in contact pressure. The terminals are 20 mm. rods, projecting 5 cm. horizontally in front of the wall of the cabinet; at the back, the middle electrode (anode) is connected with one pole of the current, and the two outer ones (cathodes) with the other pole.

The ore, weighed into a tall battery-beaker of 100 cc. capacity, is digested with ten cc. of nitric acid. The lead sulphate formed is readily dissolved after boiling by the addition to the beaker of from ten to twenty cc. of a saturated solution of ammonium nitrate containing twenty per cent free ammonia. After solution, the beaker is nearly filled with water, and from ten to twenty cc. nitric acid added. The solution is now ready for electrolysis. A wide range of current strength is permissible, but from 1.5 to 2 amperes is most satisfactory; this amount keeps the solution sufficiently hot during the electrolysis. At the end of two hours the lead is completely deposited in the form of peroxide on the anode. The anode is then removed, washed in water and in alcohol, ignited, and weighed. The theoretical factor is

0.866, but in practice 0.855 is found to be more accurate, probably due, as Holland says, to an excess of oxygen in the peroxide.

The accuracy of this method ranks with that of carefully made electrolytic coppers, and its advantage is the small amount of the chemist's time required. In the presence of manganese or antimony it is necessary to have a large excess of free nitric acid in the electrolyte, under which condition neither element interferes. Bismuth, even in the presence of very large amounts of free nitric acid, is partly precipitated as bismuth oxide with the lead. Its presence can be recognized by a light-blue color given to the peroxide coat. Arsenic and tellurium have to be removed before electrolysis, for, if present in large amounts, they effectually prevent any deposition of lead. Unless the anode is sand-blasted, only a comparatively small amount of peroxide will adhere, but, properly sand-blasted, adherent deposits of 250 mg., and even up to 600 mg., of peroxide may be obtained in daily work.

In weighing the pulp, weigh off 855 mg., which has been christened a "plum," and multiples thereof, in order to avoid the necessity of calculating each result, the weight of peroxide found being called lead.

**164. Low's Chromate Method.\*** Prepare an "extraction solution" by mixing one part of cold saturated solution of commercial sodium acetate with two parts of water, and add ten cc. of 80 per cent acetic acid per liter. Use hot in a wash bottle.

Take half a gram of the ore and treat it by the usual methods to obtain lead as lead sulphate on the filter. After the lead sulphate is properly washed, place a clean

\* Western Chemist and Metallurgist, Dec., 1909.

beaker under the funnel, and dissolve all of the lead sulphate on the filter with the boiling hot "extraction solution." After dissolving all of the lead sulphate, add from a small pipette just enough of a 12 to 15 per cent solution of sodium hydroxide to form a slight permanent cloudiness, after which add just enough acetic acid to clear the solution; a single drop is usually enough. If the ores are very low grade, it is necessary to use phenolphthalein as an indicator, since a cloud might not be formed.

Now add ten cc. of a five per cent solution of potassium dichromate; heat to boiling, and boil for one or two minutes, or until the precipitate becomes of a deep orange color and settles fairly well on removing from the heat. Filter through a 11-cm. filter, and wash ten times with a hot dilute solution of sodium acetate. After thorough washing, place a 350-cc. flask under the funnel, and dissolve the precipitate with cold dilute hydrochloric acid (one part of acid to two parts of water) using it from a wash bottle.

Dilute the filtrate in the flask with cold water until it is nearly two-thirds full, and add two cc. of a 50 per cent solution of potassium iodide. Mix and titrate without delay with standard sodium thiosulphate solution until the brown color becomes faint; then add sufficient starch solution to produce a strong blue color, and finish the titration very slowly, finally, a drop at a time, allowing each drop to produce its full effect, until the solution becomes a clear pale green with no tinge of blue. The end point is sharp, but care must be exercised or it may easily be passed by a drop or two.

Standardize the thiosulphate on pure lead, weighing off about two-tenths of a gram of pure lead foil, dissolving it in nitric acid, and precipitating as lead sulphate, following the method for ores. The thiosulphate solution used

for copper may be employed, and the lead factor calculated by multiplying the copper value by 1.069.

I have not had time to try this method out, but Mr. Low's work is always good, and my brother, F. H. Seamon, has tried it out and tells me he thinks well of it.

**165. Valuation.** As a rule lead is not paid for when the percentage is less than five per cent. When over five per cent all of the lead is paid for. When lead is selling for \$4.00 per 100 lbs. in New York, twenty-five cents is paid for each unit. For every variation of five cents in the New York price of lead, one cent per unit is added or deducted.

The smelting charge is usually \$3.00 per ton with the usual deductions for silica and payments for such iron and lime as may be present. Local smelting conditions sometimes enable the producer to secure better terms.

In Mexico the value of lead ore is based upon the selling price of lead in the London market. When lead is worth £13 per long ton in London the smelters pay nine-tenths of one cent (U. S. currency) per pound for each pound of lead in the ore; for each variation of 1s. 3d., add or deduct  $1\frac{1}{2}$  cents (U. S. currency) per 100 lbs.



## CHAPTER XIII

### MAGNESIUM

**166. Detection.** There is no quick simple test for the detection of magnesia, and the reader is referred to any of the standard methods for qualitative analysis.

**167. Decomposition.** The compounds of magnesia met with in technical work are all easily decomposed by the ordinary acid treatment, so no special instructions are here needed. All lime, lead, copper, iron, zinc, aluminum, and other metals of the third, fourth, fifth, and sixth groups must be removed from the solution before magnesia can be safely precipitated.

**168. Precipitation.** The solution properly prepared is made alkaline with ammonia water and boiled down to small bulk, and a solution of sodium ammonium phosphate, 160 grams to the liter, is added drop by drop, until all is precipitated. The solution is then allowed to stand until cooled, when twenty cc. of ammonia water are added, and after standing a few hours longer, the precipitate is filtered off and washed with ammonia water of about two to three per cent strength. The filter and precipitate are dried, and the precipitate transferred to a weighed platinum crucible. The filter paper is wrapped about with platinum wire and separately ignited, the white, or grayish, ashes being dropped into the crucible. The crucible is then gently heated, and finally ignited to red heat, when it is weighed. The increase in weight is

due to  $\text{Mg}_2\text{P}_2\text{O}_7$ . This weight multiplied by 0.3624 will give the weight of magnesia,  $\text{MgO}$ .

Magnesia determinations are seldom called for, consequently it is not considered worth while to go into further details.

## CHAPTER XIV

### MANGANESE

**169. Ores.** There are quite a number of oxides of manganese occurring in sufficient abundance to constitute ores, chief of which may be mentioned pyrolusite, psilomelane, and braunite.

**170. Detection.** Heat a small portion of the finely powdered mineral on a piece of platinum foil with four times its bulk of a mixture of equal parts of sodium carbonate and potassium nitrate. The fused mass will turn a bluish green if manganese be present.

**171. Methods.** Manganese is usually determined by the Volhard method in smelter practice, but I find that it usually gives a lower result than the actual content of manganese. A better method, in my opinion, is the oxalic acid method, but I find it also somewhat unsatisfactory, frequently too high. The reactions in both of these volumetric methods are based upon the precipitation of manganese in the tetravalent form. It is well known that this precipitate is composed of manganites and hydroxides, and it seems to me that the variations in results must be partly due to the fact that all of the manganese is not precipitated in the tetravalent form. I describe both methods because they are standard and seem firmly established, but when I want an accurate and reliable determination I resort to the gravimetric method, which under ordinary laboratory conditions is usually rapid enough.

**172. Decomposition.** A half a gram of the ore is heated with seven cc. of concentrated hydrochloric acid in a No. 2 casserole, with the addition of five cc. of nitric acid in the case of sulphide ores. After decomposition is completed and the acids boiled down to near dryness, nearly an excess of sodium carbonate is added, the solution is boiled, and then an excess of zinc oxide is added, throwing down the iron, alumina, and other interfering metallic oxides, except the manganese and zinc. This precipitate is filtered off and washed with hot water. Five grams of sodium acetate are then added with fifteen cc. of bromine water, or more if there is a large quantity of manganese present, then three cc. of ammonia water and five grams of ammonium chloride, and the solution boiled, resulting in the precipitation of the manganese oxide. This is then filtered off and washed thoroughly with hot water.

**173. Gravimetric Method.** The precipitate of manganese oxide is then ignited in an annealing cup and weighed as  $Mn_3O_4$ . Multiply this by 0.7205 to obtain the weight of manganese, from which the percentage is readily calculated. It is necessary to be careful in washing this precipitate, if the gravimetric method is employed, to insure washing out all of the sodium salts, some of which is apt to be held by the gelatinous precipitate and would thereby increase the amount of manganese found. The results are accurate and the method is particularly valuable in the case of small percentages of manganese.

**174. Volhard's Method.** Treat half a gram of the ore in a No. 3 casserole with seven cc. of concentrated hydrochloric acid and five cc. of strong nitric acid, employing heat finally to complete decomposition. Then add seven cc. of strong sulphuric acid, and boil hard until strong fumes of sulphuric acid are given off, cool, add twenty-five cc. of water, and wait till all of the ferric sulphate

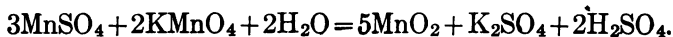
present dissolves. Then add a suspension of zinc oxide in excess and boil again until the iron is precipitated. Filter, and wash well with hot water.

It is customary to transfer the sulphuric acid solution to a 500-cc. flask, graduated, before adding the zinc oxide, then diluting up to the 500-cc. mark, and withdrawing, after the solution has settled clear, 100 cc. with a pipette.

**175. Titration with Permanganate.** The clear solution is placed in a 500-cc. flask with three drops of nitric acid, and heated to boiling. Then run in a standard solution of potassium permanganate until, on standing, after re-boiling, there is a permanent pink color. If the analyst knows approximately the amount of manganese in the pulp, he runs in nearly the maximum amount and then slowly finds the exact point. In this way the method is most reliable. But, when this is not known, the method becomes tedious, and as the time for each settling must be allowed, the analyst is apt to become tired and consider the end-point attained before it is actually reached. When small amounts of manganese are present too high a result is often attained. The final end-point is best observed by holding the flask against a pure white background, when the pink color may most quickly be seen.

The permanganate solution used for iron is generally employed, and the manganese factor is obtained by multiplying the iron factor by 0.2952. This factor multiplied by the number of cc. used of the permanganate solution gives the weight of manganese, which must be multiplied by five if the ordinary method is used of withdrawing a fifth part of the solution with a pipette.

**176. Chemistry.** The reaction is expressed by the following equation:



In the presence of lime and zinc, various manganites may be formed, but it is generally believed that the manganese precipitated is always in the tetravalent form, which, if true, requires no change in the factor.

My experience with this method has been unsatisfactory, and while I have, at times, obtained accurate results in working with substances in which the exact amount of manganese was known I find it too uncertain, slow, and tedious, particularly when there is a large percentage of manganese present and the analyst does not know beforehand approximately the amount of manganese present.

**177. Oxalic Acid Method.** In this method the ore is treated precisely as in the Volhard method, including the treatment with zinc oxide. The zinc oxide precipitate is filtered off, or one-fifth of the solution is withdrawn with a pipette as in the Volhard method, 174.

The solution is treated in a flask with five grams of sodium acetate and 25 cc. of bromine water, and boiled for several minutes. Filter, and wash the precipitate with hot water. All fumes of bromine are removed from the flask by boiling a little water in it. The washed precipitate is put back into the flask and a measured quantity of standardized oxalic acid solution is run into the flask in excess. If the composition of the ore is known, it is best to use five, ten, twenty, fifty, or sixty cc. of the oxalic acid solution and keep the excess comparatively small. Then add fifty cc. of a ten per cent solution of sulphuric acid, and heat the mixture to near the boiling-point, being careful not to shred the filter.

Then dilute the solution to 200 cc. with hot water, and determine the excess of oxalic acid by running in a standard solution of potassium permanganate to the first permanent pink color in the warm solution. Subtract the excess of oxalic acid found from the amount used,

and multiply the number of cc. thus found by the value of one cc. in manganese, and calculate the percentage in the usual way.

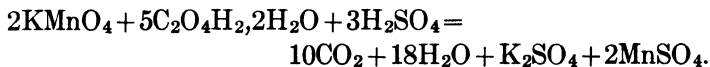
**178. Standardizing.** 11.46 grams of crystallized oxalic acid are dissolved in one liter of water to obtain a solution of which one cc. will equal, approximately, 0.005 gram of manganese.

It is customary to use the permanganate solution employed for iron, in which case its strength is determined by weighing up 0.2 gram of pure oxalic acid and dissolving it in a flask with one hundred cc. of ten per cent sulphuric acid. Heat to 60–70° C. and run in the permanganate to the first faint pink which is permanent. The standard solution of oxalic acid must also be run with the permanganate solution in like manner.

**179. Chemistry.** The reaction of the oxalic acid with the precipitated manganese oxide is:



Between the permanganate and oxalic acid it is:



**180. Valuation.** In the lead-silver smelters the manganese is paid for at the same rate as for iron, viz., five cents per unit.

In the manufacture of ferromanganese to be employed in the manufacture of steel, large quantities of manganese are consumed. Ores to be employed for this purpose should have a content of not less than 40 per cent of manganese. They are paid for f.o.b. Chicago, at the rate of thirty cents per unit, provided there is not more

than eight per cent silica, or more than 0.25 per cent of phosphorus, and the manganese content is 49 per cent or over. Complying with these conditions, 49 per cent ore is worth \$14.70 per ton, with thirty cents added for each unit in excess of 49. Falling below 49 per cent and not going below 40 per cent, twenty-seven cents per unit is paid. A deduction of fifteen cents per unit is made for each per cent of silica above eight per cent, and there is no demand for manganese ores carrying more than twelve per cent of silica and 0.27 per cent of phosphorus.



## CHAPTER XV

### MERCURY

**181. Ores.** Cinnabar, the sulphide of mercury, is the principal mineral in the mercurial ores. It is more or less associated with secondary minerals, which occur near the surface.

**182. Detection.** Treat the finely divided pulp with five cc. of concentrated hydrochloric acid, boiling for a few minutes. Then dilute with water and filter. Place a small piece of sheet aluminum in the solution and boil for a few minutes, cool, and remove the aluminum. Mercury will show itself by its bright lustre, unless in very small amounts, and by the aluminum becoming quite warm on removal from the cold liquid and forming a white incrustation varying in amount with the amount of mercury present. This test I have found characteristic and sufficiently delicate, showing when there was only two milligrams of mercuric chloride in 100 cc. of solution.

**183. Methods.** Mercury is generally determined in technical work by the dry method. The following volumetric method, originated by me, has given satisfactory results for more than a year past on mercurial ores, with an iron, lime, clay, gangue, and I think it will prove satisfactory with other gangues; I recommend it.

**184. Decomposition.** Weigh out half a gram of the finely ground pulp into an Erlenmeyer flask of 125 cc. capacity, add five cc. of concentrated hydrochloric acid, and after allowing it to act for about ten minutes at a

temperature of about 40° C., add three cc. of concentrated nitric acid; in about ten minutes decomposition of the ore will be complete, so far at least as to have the mercury in solution. Then add five cc. of concentrated sulphuric acid, if lead be present, then add 15 cc. of water, and then add ammonia cautiously until the liquid is slightly alkaline, when bismuth, if present, will precipitate; make feebly acid with nitric acid, filter, and wash well, collecting the filtrate in a beaker.

**185. Titration.** Add one cc. of nitric acid that has been made brownish in color by exposure to the light, and run in a solution of potassium iodide (8.3 grams to the liter) until a drop of the liquid brought into contact with a drop of starch liquor, on the spot plate, shows a faint bluish tinge. I generally set one-third of the solution aside, and after running to a strong end reaction, add the reserved portion and run slowly to the end-point, finally rinsing out the vessel that holds the reserve. Deduct one-half a cc. from the burette reading and multiply by the strength of the standard in mercury per cubic centimeter, and calculate the percentage in the usual way.

The potassium iodide solution should be standardized by weighing off pure mercuric chloride and titrating as above, previously adding two cc. of the discolored nitric acid. Using 8.3 grams of potassium iodide to the liter, one cc. will be found equivalent to 0.005 gram of mercury.

In titrating, the characteristic red precipitate of mercury iodide will be obtained unless the amount of mercury present is very small. Although the precipitate may not be formed, I have not found that it made any difference, as the blue color will not appear until there is an excess of potassium iodide.

Iron, copper, bismuth, antimony, and arsenic did not

affect the results when added separately to the pulp containing mercury. Silver salts, if present, alter the results. I have found the method accurate to one-tenth of one per cent.

(Since this article was sent to the printer I have been trying out the method, using solutions of cadmium iodide and zinc as substitute for potassium iodide. I have not completed my tests, but so far as they go the substitution appears to be an improvement.)

**186. Gravimetric Method.** Eschka's method I have found reasonably reliable. Mix half a gram of the ore with two to three grams of fine iron filings in a porcelain crucible. Cover the crucible with a weighed piece of sheet silver or gold in such a way as to make a dish-like depression, in which water can be kept to cool the metal sheet. Care must be taken that the crucible is well covered. Place the crucible in a hole made in asbestos board, and made to fit so the bottom of the crucible only will be heated. Add cold water from time to time to the cover and heat gently for about thirty minutes. Dry the cover without employing heat, and weigh it. The increase in weight is due to mercury.

**187. Valuation.** The ores of mercury are generally low grade and cannot be readily concentrated. The smelting is simple and the cost of the plant small, increasing proportionately to the quantity of ore smelted. Consequently, there is no market for mercurial ores, which are smelted at or near the mines.

Commercial quicksilver is worth from \$40.00 to \$45.00 per flask of 75 lbs.

## CHAPTER XVI

### MOLYBDENUM

**188. Ores.** Molybdenite, the sulphide of molybdenum, is the only important ore; but wulfenite, the molybdate of lead, is sometimes found in large quantities.

**189. Detection.** Place a few drops of sulphuric acid in the bowl of a platinum spoon, or in a depression on a piece of platinum foil. Place some of the finely powdered mineral on the top of the acid, and heat until fumes of sulphuric acid come off copiously. Cool, and then breathe upon the test, when an intensely blue color will appear if molybdenum is present. Heat, or much water, destroys the color.

**190. Decomposition.** One-half a gram (or more if the per cent is small) of the finely powdered ore is digested with twenty cc. of concentrated nitric acid in an Erlenmeyer flask, for one hour; water is then added, and after allowing the solution to settle clear, it is decanted and the residue again digested with ten cc. of concentrated hydrochloric acid. The molybdenum oxide, mixed with tungstic acid, silica, and possibly lead and barium sulphates and tin oxide, will remain undissolved. The acid is decanted and the residue washed with hot water.

Ammonia water, moderately dilute, is then poured into the flask to dissolve the molybdic oxide. The ammonia will also take up any tungstic oxide. The ammonia solution is evaporated to dryness in a weighed platinum dish, washed once with dilute alcohol, and again evaporated to dryness. It is then cooled and weighed as  $\text{MoO}_3$ .

Multiply this weight by 0.6667 to find the weight of molybdenum. If tungstic acid is present, the result by this method will be much too high.

**191. Volumetric Method.** The ammoniacal solution of molybdenum is neutralized with nitric acid. The solution is evaporated nearly to dryness, and a solution of lead acetate is added in excess. The precipitate will be lead molybdate mixed with lead tungstate. This is filtered off and ignited at a low heat, in a strong current of air, to prevent fusion of the mass. It is then transferred to a beaker, concentrated hydrochloric acid added, and heated nearly to boiling, when it is diluted with water and filtered off and washed. The tungstic acid is on the filter, and it may be set aside for the determination of that substance. The filtrate containing the molybdic acid is then boiled with zinc until it is completely reduced, when five cc. of sulphuric acid are added, the liquid diluted to 700 cc. and allowed to cool to room temperature, when the zinc is removed and the solution titrated with potassium permanganate to end reaction. The solution for iron may be employed, and the factor for molybdenum calculated by multiplying the iron factor by 0.5729.

**192. Evans' Method.\*** This method has for its object the determination of molybdenum in wulfenite or other ores containing lead.

**193. Decomposition.** From one-half a gram to five grams of the finely divided pulp are attacked with hydrochloric acid, and nitric acid is afterward added and heat applied until all of the soluble constituents of the ore are in solution; after one or two evaporations with nitric acid to expel all chlorides, the mixture is cooled, diluted with distilled water, and a slight excess of ammonia water

\* Western Chemist and Metallurgist, Vol. III, p. 218.

is added. Ammonium sulphide is then added, drop by drop, and when all of the iron, lead, etc., is converted into sulphides, a few cc. excess are added, and, after stirring, the mixture is allowed to stand in a warm place until all the iron and lead sulphides has settled. It is then filtered, and the residue washed with a solution containing a slight amount of ammonium sulphide.

The precipitate is dissolved in a hot mixture of equal parts of nitric acid and bromine water, and the iron and lead re-precipitated with ammonium sulphide to ensure the removal of all molybdenum, and filtered as before.

The combined filtrates, which will show a deep brown color if much molybdenum is present, are slightly acidified with hydrochloric acid, and a rapid stream of hydrogen sulphide gas passed in for a few moments. The molybdenum sulphide is filtered off, and washed well with hot dilute hydrogen sulphide water. The precipitate is then rinsed into a No. 2 beaker, and a few cc. of a hot mixture of nitric acid and bromine water poured onto the paper, receiving the acid and washings in the beaker in which the molybdenum sulphide was originally precipitated. This is then boiled with frequent additions of bromine water to oxidize the free sulphur and ensure complete solution.

**194. Gravimetric Method.** Any unoxidized sulphur is filtered off; after careful washing, ammonia is added just to neutralization, using litmus paper as an indicator. A few drops of acetic acid are then added, and afterwards a slight excess of a solution of lead acetate is added and the resulting lead molybdate, after stirring well and allowing to settle, is filtered through a tared Gooch crucible or a counterpoised filter paper, washed thoroughly with hot water, and dried at  $100^{\circ}\text{C}$ . to constant weight. The weight of the lead molybdate multiplied by 0.2614 equals

the weight of metallic molybdenum present, from which the percentage may be easily calculated.

**195. Volumetric Method.** After the solution of the molybdenum sulphide it is unnecessary to filter off any free sulphur present. The solution is almost neutralized with ammonia water, then made barely acid with acetic acid, heated to boiling, and, while hot, titrated with a standard solution of lead acetate, using a dilute solution of tannic acid on a spot plate as an indicator. It is the exact reverse of the molybdate method for lead, and the lead acetate is run in until the indicator no longer gives a yellow color.

The solution of lead acetate is made by dissolving 15.7 grams of C. P. salt in dilute acetic acid and making up with distilled water to one liter. Twenty-five cc. of this solution are titrated against a standard solution of ammonium molybdate. The ammonium molybdate solution, having been standardized in terms of pure lead, the lead content of the acetate solution is shown, and the lead factor multiplied by 0.4640 gives the molybdenum value.

**196. Valuation.** Molybdenum ore guaranteed to run over 90 per cent  $\text{MoO}_3$  is worth about \$400.00 per ton. The price fluctuates very rapidly and the demand for it is not large. It is used in making certain special steels.

## CHAPTER XVII

### NICKEL AND COBALT

**197. Ores.** Millerite (the sulphide) and garnierite (a nickel magnesium silicate) are the most important sources of nickel. There is also a large deposit of pyrrhotite near Sudbury, Ont., carrying from one to nine per cent of nickel, which for some years past has been an important source of supply.

The ores of cobalt are speiss, the arsenide of cobalt, cobalt glance, the sulphoarsenide, and earthy cobalt, or wad. The new silver district in Ontario is now producing large quantities of cobalt.

**198. Detection.** A portion of the finely divided pulp is boiled with hydrochloric acid; after decomposition is effected, sodium peroxide in excess is added, and the solution filtered off from the insoluble residue and the iron hydroxide which will also contain any cobalt and nickel which may have been in the mineral tested. This precipitate is washed well with hot water, after which it is dissolved in hydrochloric acid and diluted with water. Ammonia water in excess is then added, followed by fifteen cc. of bromine water; after boiling, the solution is filtered off from the manganese and iron hydroxides. The nickel and cobalt present will be in the solution, which is acidified with hydrochloric acid, after which a solution of potassium ferricyanide is added, followed by addition of ammonia water in excess. Any cobalt present will be precipitated by this treatment, and



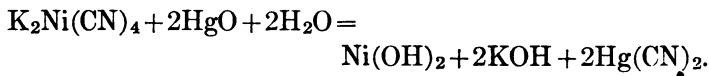
the precipitate will have a bluish color; it is filtered off, and the solution will be brownish yellow in color if nickel is present.

**199. Consideration.** Methods for the determination of nickel must always take into consideration the presence of cobalt, as the chemical properties of these two metals are very similar, and the metals are apt to occur associated.

**200. Decomposition.** A half gram, or more, of the finely divided pulp is treated in a No. 2 casserole with ten cc. of concentrated hydrochloric acid, and after this has acted for some minutes, five cc. of nitric acid are added, and the solution evaporated to dryness. It is then treated with five cc. of concentrated hydrochloric acid, and water is added, after which the insoluble residue is filtered off and washed. The filtrate is collected in a beaker and sodium peroxide added in excess, after which the solution is boiled. It is filtered while hot, and the residue washed with boiling water. The precipitate is dissolved in hydrochloric acid, diluted with water, and five grams of ammonium chloride are then added, after which ammonia water in excess is added, followed by fifteen cc. of bromine water. The solution is then boiled, and the iron and manganese hydroxides are filtered off and washed with hot water. The filtrate contains the nickel and cobalt. Make the solution feebly acid with hydrochloric acid, and add a slight excess of potassium hydroxide and boil. The nickel and cobalt are precipitated together and filtered off. After they are thoroughly washed with hot water, the precipitate is ignited and weighed; from the weight the combined percentage of nickel and cobalt may be calculated.

**201. Determination of Nickel.** If the nickel is to be determined separately, the hydroxide precipitate men-

tioned in the preceding paragraph is not ignited, but while still moist it is transferred to a No. 3 casserole with the aid of water, and about three grams of potassium cyanide are added and the solution is heated for the space of one hour. An excess of precipitated red mercury oxide is then added, and the solution boiled for thirty minutes, causing the nickel to precipitate as the hydroxide, but carrying mechanically some of the mercury cyanide. The reaction is as follows:



The solution is filtered, and the filtrate set aside for the determination of cobalt, while the washed precipitate is ignited in an annealing cup in a muffle with a strong draft to carry off any poisonous fumes of mercury, then cooled, and weighed as NiO. Multiply the weight by 0.7857 to obtain the weight of nickel.

**202. Determination of Cobalt.** Take the filtrate from the nickel hydroxide and add nitric acid until nearly neutral, leaving the solution faintly alkaline. Add a solution of mercurous nitrate so long as a precipitate forms; then filter off the precipitate of mercurous cobalticyanide, wash well, and ignite in an annealing cup as with the nickel precipitate, and weigh the  $\text{Co}_3\text{O}_4$ . Multiply by 0.7345 to obtain the weight of cobalt.

**203. Uses and Valuation.** Nickel is used principally for plating iron and brass; also for small coins and for the manufacture of nickel steel which has certain valued special applications.

Nickel ores carrying eight per cent of the metal are worth about \$29.00 per ton at the shipping point, less the freight charges to the smelting works. For each

per cent of nickel above the eight per cent the value increases at the rate of two dollars and fifty cents per ton.

Cobalt is used principally for the manufacture of smalt, a silicate of cobalt and the alkalies, which has an intensely blue color and is much valued for pigments.

Cobalt ores carrying three per cent of cobalt are worth \$100.00 per ton at smelting point, and for each per cent in excess of three there is an increase in value of twenty-five dollars per ton.

In the handling of the high-grade silver ores of Ontario which carry cobalt, the smelters pay ten dollars per ton for all ores carrying from six to eight per cent of cobalt; twenty dollars for the ores running from eight to twelve per cent and thirty dollars for all ores carrying more than twelve per cent, in addition to payment for the silver content of the ores.

## CHAPTER XVIII

### PLATINUM

**204. Ores.** Most of the metallic platinum of commerce is secured from placer deposits; and black sands, found in erosion districts, may have platinum enclosed. Sperrylite, an arsenide, has also been found in quantity sufficient to become an ore of platinum.

**205. Detection.** The reaction of solutions of platinic salts with potassium iodide is given in the recent standard works on analysis as a reliable test for platinum. I published this reaction in 1893, believing it to be reliable, and the method has been generally adopted by various authors, usually without giving credit. In recent years I have had occasion to examine this method again, and I find that the purple coloration has no connection with the presence of platinum, but is due entirely to the formation of free iodine by minute traces of chlorine. It is very difficult to secure a solution of platinum without having a minute trace of chlorine in the solution. Eliminate this trace and all other substances that decompose potassium iodide and no reaction will be given with platinum salts.

The only reaction for platinum that can be relied upon is to concentrate on a water bath the solution, to which a little ammonium chloride has been added; if any yellow crystals are formed, filter them off, wash with alcohol, and ignite the dried precipitate in an annealing cup, when the characteristic white metal will be obtained.

**206. Determination.** If platinum occurs in any mineral which is assayed for silver or gold, the platinum will all be found in the silver button remaining after cupellation. As the platinum is usually small in amount, it is best to unite the silver beads obtained by assaying several half assay ton charges of the ore.

These silver beads are boiled with sulphuric acid until all of the silver has been dissolved out; no nitric acid may be used, as some platinum, when alloyed with silver, goes into solution with nitric acid. Any blackish residue remaining after treatment with sulphuric acid may be gold and platinum. After removal of the silver, the liquor is decanted and the residue washed with distilled water. The residue is then treated with chlorine water until it dissolves. The clear solution, made so by filtration, if necessary, is then evaporated to syrupy consistency in a glass vessel heated in a water bath. A small amount of ammonium chloride solution is then added, and the evaporation continued to soft dryness. Diluted alcohol (50%) is then placed on the mass, and when liquid, the yellow crystals of ammonium platinic chloride are filtered off; the precipitate is dried, ignited, and weighed as metallic platinum.

This method does not allow for the possible presence of ruthenium and rhodium. Should platinum be found, it may then be necessary to learn whether it is pure, or alloyed with other metals of the platinum group. In that event refer to Crooke's "Select Methods in Chemical Analysis," p. 437, et seq.

**207. Valuation.** Platinum sells when pure for from \$18.00 to \$35.00 per ounce troy. The price has fluctuated very much during recent years.

**208. Uses.** Platinum is employed chiefly for vessels and weights of precision used in scientific operations.

## CHAPTER XIX

### POTASSIUM AND SODIUM

In the analysis of clays and cements it is sometimes necessary to determine these alkalies.

**209. Method of J. Lawrence Smith.** The substance is heated with a mixture of one part of ammonium chloride and eight parts of alkali-free calcium carbonate. Half a gram of the mineral is intimately mixed with four grams of the mixed calcium carbonate and ammonium chloride, and transferred to a platinum crucible. The heat should first be applied very gently so as to cause the formation of hydrochloric acid; after about fifteen minutes the heat is increased, and finally the temperature is raised to a dull red heat so the mass will sinter, being careful that actual fusion does not occur. After cooling, the sinter is removed and boiled with 75 cc. of pure water. The clear solution is passed through a filter. The solution is then treated with ammonia and ammonium carbonate to precipitate the lime. The filtrate is evaporated to dryness, and the residue treated again with ammonium carbonate, and again filtered off. This filtrate is evaporated to dryness and the ammonium salts driven off. The mass is then treated with a few drops of hydrochloric acid so as to moisten the residue with the acid, and after evaporation to dryness the weight is determined; this will represent the amount of sodium and potassium chloride. The potassium is determined by treating the residue with a small amount of alcohol and water. Plati-

num chloride is added in excess and everything evaporated to dryness on a water bath. Take up with dilute alcohol, and filter off the platinum chloride through a tared filter, wash it with alcohol, carefully dry, and weigh. The weight of platinum chloride is multiplied by 0.3054 to obtain the weight of KCl. The NaCl is found by subtracting the weight of potassium chloride from the total weight of the KCl and NaCl.

## CHAPTER XX

### TIN

**210. Ores.** Cassiterite, the oxide, is the mineral that furnishes the principal ore supply of tin. Another mineral carrying tin is stannite, the sulphide, but it does not occur in sufficient quantity to be considered an ore.

**211. Detection.** Fuse the finely powdered mineral with a mixture of dry powdered potassium cyanide and sodium carbonate on a piece of charcoal, with a strong reducing flame produced by a blowpipe. Metallic globules of tin will separate, and these can be dissolved in concentrated hydrochloric acid; to the solution a solution of gold chloride may be added, when the formation of a purple red coloration or a brownish precipitate of metallic gold will furnish a characteristic and delicate reaction that cannot be mistaken.

**212. Methods.** The old methods for the determination of tin generally advise concentration by panning, but there is really no need for this inaccurate work. The ores should be very finely powdered. It is very difficult to dissolve the oxide of tin with acids, but the following fusion method will give a soluble compound that can be readily handled.

**213. Decomposition.** Mix half a gram of the pulp with five grams of sodium peroxide in a porcelain crucible, and heat till fusion is clear. If the ore is low grade, it is well to take a larger quantity, increasing the amount of sodium peroxide. The tin forms sodium stannate.



On cooling, put the crucible in a No. 3 casserole and boil with hot water to disintegrate the mass. Acidulate with hydrochloric acid, and filter off from any residue. Although decomposition is usually complete on the first fusion, it is best to examine the residue to ensure perfect decomposition, repeating the fusion if necessary.

**214. Gravimetric Method.** Boil the acidulated solution with a V-shaped piece of metallic aluminum, when the tin will be completely precipitated as a spongy mass, which can be readily separated from the aluminum and then dried and weighed as metallic tin. This method is inaccurate if any other metals are present which go into solution and are precipitated by metallic aluminum. The volumetric method is generally more satisfactory.

**215. Volumetric Method.** The acidulated solution formed in decomposition with sodium peroxide is placed in a flask and pure iron wire added; the flask and its contents are then boiled for about thirty minutes to reduce all the tin to the form of stannous chloride. The flask is then cooled to room temperature, the iron wire is next removed, a little starch solution is added, and the solution titrated with a standard iodine solution.

**216. Standardization.** The standard solution of iodine is made by dissolving 9.7 grams of iodine in a little water with the addition of fourteen grams of potassium iodide, and diluting to one liter. This should give a solution of which one cc. is equal to 0.005 gram of tin.

The solution is standardized by dissolving one-tenth gram of pure tin in hydrochloric acid, adding iron wire, and boiling for thirty minutes. Then cool to room temperature, remove the iron wire, add starch solution, and run in the iodine solution to the first permanent pink coloration. Divide the weight of tin used by the cc. of iodine solution run in. This method is reasonably accurate.

**217. Uses and Valuation.** Tin is used mainly for tinning iron sheets which are employed for roofing and for various other purposes.

The tin smelters require that the ores should be well concentrated previous to purchase, consequently there is no market for ores carrying less than fifty per cent of metallic tin. The price paid varies with the nature of the impurities, but the producer usually receives three-fourths the selling price of metallic tin for each pound of tin in his ores.

## CHAPTER XXI

### TUNGSTEN

**218. Ores.** Hubnerite, or manganese tungstate with iron, and scheelite, calcium tungstate, are the chief minerals constituting ores.

**219. Detection.** Fuse a portion of the powdered substance in a platinum spoon, or on a piece of platinum foil, with potassium disulphate. Put the fused mass in a test tube with a solution of ammonium carbonate, and filter if necessary.

To the clear solution add a few drops of stannous chloride, then enough hydrochloric acid to acidify the liquid, and heat gently, when a beautiful blue color will be produced. This is a characteristic and delicate test.

**220. Reporting Results.** The determination of small quantities requires the greatest possible care. The results are usually reported as tungstic acid,  $\text{WO}_3$ .

**221. Decomposition.** Decompose one-half gram or more of the ore as described in 190, and carry out all the operations described therein. The residue will be  $\text{WO}_3$  mixed with  $\text{MoO}_3$  (if present).

Molybdic oxide is removed with hydrochloric acid as described in the same section.

The residue on the filter is removed and treated with two to three cc. nitric acid. It is then diluted with 150 cc. dilute hydrochloric acid (three of water to one of acid), the solution is boiled, and the  $\text{WO}_3$  filtered off, washed, and weighed. Multiply this weight by 0.793 to obtain the weight of tungsten.

**222. Hydrofluoric Acid Method.** Weigh out half a gram of the very finely powdered ore into a platinum dish, and digest with a mixture of equal parts of hydrofluoric and hydrochloric acids at a low heat. Finally, after solution is effected, evaporate nearly to dryness, adding towards the last fifteen cc. of concentrated hydrochloric acid. Transfer the solution and residue to a 200 cc. Erlenmeyer flask. Ten cc. of concentrated hydrochloric acid and ten cc. of concentrated nitric acid are then added, and all boiled down to a volume of ten cc. to drive off the last traces of hydrofluoric acid and to convert the tungsten into  $\text{H}_2\text{WO}_4$ .

Fifty cc. of hot water are then added, and the solution is gently heated for about thirty minutes, when it is filtered off; the tungstic acid is dissolved with warm dilute ammonia water and filtered, receiving the filtrate in a weighed platinum dish. Evaporate to dryness at gentle heat, cool and weigh. The residue should be yellow in color if it is pure  $\text{WO}_3$ .

**223. Tungstic Acid in Low-grade Tungsten Ores.\*** The charge may be from 5 grams upwards, or better 5.6, 11.12, 16.8 or any convenient multiple of 2.8, so that the milligrams of tungstic acid obtained represent simple ratios of 1 pound  $\text{WO}_3$  per ton of ore (long ton); 2.8 grams (or multiple) is taken because only four-fifths of the solution is used for the actual assay, i.e., it is a convenient sort of "assay ton" for pound per ton of 2240 pounds under the special conditions of the assay. The charge is digested in a four-inch porcelain dish with twenty cc. of a 25 per cent solution of sodium hydroxide (free from chloride) on a water bath for thirty to forty-

\* The Mining World, by H. W. Hutchin and F. J. Tonks, June 12, 1909, p. 1123.

five minutes. The assay is next diluted, a little sodium peroxide added to oxidize any decomposition products of sulphides, then transferred to  $\frac{1}{2}$ -liter flask, and diluted to 250 cc.; 200 cc. of a filtered portion are first acidified with nitric acid, then made alkaline with ammonia. The assay is brought to the boiling-point, filtered and washed. The filtrate is made slightly acid with dilute nitric acid, and mercurous nitrate solution added in excess followed by a few drops of dilute ammonia. On warming and stirring, the precipitate settles readily. After filtering and washing the precipitate with weak mercurous nitrate solution, the paper and precipitate are ignited together in a porcelain crucible, or, if the ore is free from arsenic in a platinum crucible. Weigh as tungstic acid; with a charge of 5.6 grams, the milligrams obtained, divided by two, give pounds  $\text{WO}_3$  per ton.

For assays of ores and tailings the sample may be reduced to sufficient degree of fineness in a wedgewood mortar, but for concentrates an agate mortar is necessary; fine powdering is essential. Twenty cc. of a 25 per cent solution of sodium hydroxide are sufficient to decompose charges containing not more than 0.4 gram of tungstic acid. The attack with  $\text{NaOH}$  is rapid under these conditions; 0.4 gram of tungsten concentrate being decomposed in fifteen minutes to the extent of 98 per cent of its tungstic contents, but, as a rule, from thirty to forty-five minutes are given.

**224. Strength of Mercurous Nitrate Solution.** The solution may be conveniently prepared from mercury. From two to three ounces of mercury are digested in a large beaker or flask with 25 cc. of nitric acid (sp.gr. 1.4), and 75 cc. of water on a hot plate, near boiling-point, for one and one-half hours, and left on the hot plate over night. The extract, diluted to about 400 cc., will give

a saturated solution with the minimum of free acid; 20 cc. are sufficient for most assays.

When a porcelain crucible has (from presence of arsenic in the ore) necessarily to be used, it is advisable to burn a batch of precipitates one after the other, and at the end transfer the accumulated tungstic acid to a platinum crucible for treatment with hydrofluoric acid. The loss with hydrofluoric acid is usually very small, e.g., on three assays of mineral from the battery working with a charge of 5.6 grams, the total loss was 0.5 mg.; equivalent to 0.08 pound per ton on each assay.

**225. The Action of Sodium Hydroxide on Mispickel.** In working the assays by the NaOH digestion method, a yellow colored solution was always obtained when mispickel was present, the richer the sample in mispickel the more pronounced being the color. Dilution and addition of a little sodium peroxide removed the color, the change being accompanied by a small precipitate of ferric hydroxide. In the first instance, in seeking for evidence of attack of mispickel by NaOH, the alkaline liquors were tested for sulphide with lead acetate, and were found to be free, but as it is more than probable that iron sulphide would be formed in the first stage of attack, the test was not conclusive. Using magnesia mixture, arsenic was detected in the assay liquors; the precipitate of silica, alumina, etc., also carried small quantities of arsenic.

**226. Effect of Arsenic in the Mercurous Nitrate Method.** Two solutions were prepared:

(1) A solution of  $\text{As}_2\text{O}_5$  in dilute  $\text{HNO}_3$ , strength 1 cc. = 1 mg.  $\text{As}_2\text{O}_5$ .

(2) A solution of  $\text{WO}_3$  in dilute ammonia, strength 1 cc. = 1 mg.  $\text{WO}_3$ .

**227. The Behavior of Mercurous Arsenate on Ignition.** One hundred cc. of the arsenic solution were (after care-

fully neutralizing) precipitated with mercurous nitrate; the precipitate, after filtering, washing, and drying, was detached from the paper and ignited over a Bunsen burner in a porcelain crucible for ten minutes. The residue, which was still yellow and showed slight signs of fusion, weighed 0.2774 gram. On further ignition over a large burner, the product fused and volatilized, leaving a small whitish residue of 2.5 mg. Its appearance suggested corrosion of the crucible.

The experiment was repeated with another 100 cc., but the paper and mercurous arsenate were burned together; an ignition of five minutes over a moderate Bunsen flame was quite long enough to volatilize the product, leaving a small white infusible residue of 1.8 mg.

Forty cc. of the arsenic solution treated in the same manner left a residue of one mg.

The filter paper which is present during the ignition of mercurous arsenate, by acting as a reducing agent facilitates the decomposition and volatilization.

One hundred cc. of the tungstic acid solution treated in like manner yielded 0.0990 gram  $\text{WO}_3$ , and 0.0988 in duplicate.

**228. The Behavior of Mixed Mercurous Tungstate and Arsenate on Ignition.** The three experiments, conducted like the previous ones with arsenic, viz., paper and precipitate being burned together, show that the effect of arsenic is a negligible factor in products containing 100 lbs.  $\text{WO}_3$  per ton or less, even ignoring the correction for the residue obtained from the arsenic solution.

**229. The Separation of  $\text{As}_2\text{O}_5$  from  $\text{WO}_3$  by Magnesia Mixture.**

	IV	V
$\text{WO}_3$ solution taken.....	50 cc.	100 cc.
$\text{As}_2\text{O}_5$ solution taken.....	20 cc.	30 cc.
$\text{WO}_3$ recovered.....	0.30 gm.	0.0972 gm.

In the two experiments IV and V, the arsenic was removed by magnesia mixture previous to the determination of the  $\text{WO}_3$ .

For experiment IV the magnesia was made from ordinary calcined magnesia. The loss of 0.019 grm. of  $\text{WO}_3$  is the effect of lime contained by the magnesia.

For experiment V the magnesia mixture was made from magnesium ribbon.

As to whether the separation of  $\text{As}_2\text{O}_5$  from  $\text{WO}_3$  is actually attended with a slight loss of the latter, the authors do not feel justified in stating an opinion; further investigation was discontinued.

**230. Remarks.** The authors have found the new method exceedingly useful for assays of battery pulp and tailings. The records obtained over a long period are such as to enable the tungsten losses to be apportioned among the respective products with a degree of accuracy hitherto unattainable. The comparison of losses when crushing to different sizes is not possible, but has been attempted with success. Screening tests, whether of battery pulp or tailings, may be attempted with confidence.

**231. Uses and Valuation.** Tungsten is now in large demand for the production of steel to be used as armor plate on the new war vessels.

Tungsten ores, or concentrates, are in demand when they carry 50 per cent and over of tungstic acid. The ores are paid for at the rate of \$8.50 per unit, when the percentage is from 50 to 60 per cent, and above 60 per cent at the rate of \$9.50 per unit. Fifty per cent ore is therefore worth \$425.00 per ton, and 60 per cent ore is worth \$570.00 per ton.



## CHAPTER XXII

### URANIUM AND VANADIUM

**232. Detection.** Vanadium may be detected by fusing five grams of the material with four times its weight of sodium carbonate, and when fused adding half a gram of potassium nitrate, keeping the mass at a red heat for thirty minutes. Cool and lixivate with water, add ammonium carbonate, and boil to precipitate silica. ✓ Filter, acidulate the filtrate with hydrochloric acid; then pass hydrogen sulphide gas through the solution and filter off any sulphides. Then make alkaline with ammonia water and pass hydrogen sulphide through the filtrate, when this will turn cherry red in color if vanadium is present.

Uranium is found by treating the powdered material with nitric acid, and when decomposed, diluting with water, adding sodium carbonate in excess, and boiling. Filter off any precipitate and add sodium hydroxide to the filtrate, when a yellow precipitate will be formed, showing the presence of uranium.

**233. Determination.** The following is Engel's method, which is condensed from the *Western Chemist and Metallurgist*.

From one-half to three grams of the finely powdered material are placed in a 250-cc. flask and treated with twenty cc. of sulphuric acid (one part of acid to five parts of water), and boiled down until fumes of sulphur trioxide are given off. If organic matter is present, some nitric

acid must be added to decompose it. The solution is cooled, diluted to 100 cc., and three cc. of hydrogen peroxide added to oxidize the uranium and vanadium. An excess of sodium carbonate is then added, the mixture boiled for a few minutes, partly cooled, filtered, and the filter washed. Any precipitate formed should be redissolved with sulphuric acid, reoxidized with hydrogen peroxide, reprecipitated with sodium carbonate, and the filtrates reunited.

The filtrate is then acidified with sulphuric acid, and from a half to one gram of ammonium phosphate added; the filtrate is boiled to expel all carbonic acid, after which it is made alkaline with ammonia.

It is then boiled to expel excess of ammonia, and made freely acid with acetic acid. It is then filtered, and the precipitate is washed with a four per cent solution of ammonium sulphate. The uranium forms the precipitate of uranyl ammonium phosphate, while the vanadium goes into the filtrate.

The filtrate is treated with ten cc. of sulphuric acid, two grams of sodium sulphite are added, and the excess of sulphur dioxide is boiled off; the solution is titrated immediately, while hot, with permanganate solution. The iron factor of the permanganate multiplied by 0.9159 gives the vanadium factor.

The precipitate of uranyl ammonium phosphate is dissolved with dilute sulphuric acid, and boiled with pure granulated zinc for forty-five minutes. The solution is then decanted off, the zinc washed, and the solution titrated with permanganate solution. The iron factor of the permanganate is multiplied by 2.133 to obtain the uranium factor. Better results will be secured by diluting the permanganate so that it will be only one-half the strength usually employed for iron.

## CHAPTER XXIII

### ZINC

**234. Ores.** The chief ores of zinc are sphalerite, the sulphide; calamine, the silicate; and smithsonite, the carbonate. These occur in varying degrees of purity, and are apt to be associated with lead and copper minerals.

**235. Detection.** Mix a little of the finely powdered substance with dry sodium carbonate, place it on a piece of charcoal, and heat it with a good reducing flame from the blowpipe. A white coating will be formed on the charcoal, which when moistened with a drop of a dilute solution of cobalt nitrate will, on reheating, turn faintly green in color. This test may fail if the assayer cannot make a good reducing flame.

**236. Method.** The public assayer is presented with a peculiar proposition in making zinc determinations. When the shipper is paid for the zinc content in his ores, he wants the highest result possible, which is, of course, the true zinc content. When the shipper is selling ores to the silver smelters he is penalized at the rate of from twenty-five cents to fifty cents for each unit in excess of a stated amount, usually eight per cent. In such cases the shipper is not appreciative of good work so far as the zinc determination is concerned.

The method developed and used in my laboratory is intended to give the true zinc content, and for the past three years it has shown that it will do that. I do not recommend it to those who have to work for a lower result than the true zinc content.

Every zinc control I have made during the past three years has been umpired, and I have won every umpire; no other assayer has ever reported a higher result than mine, except in one instance, and I have not determined whether this was due to faultiness in my method, or to bad work on my part or that of the umpire assayer. Probably it was due to carelessness on my part.

**237. Decomposition.** One-half a gram of the ore is placed in a No. 2 casserole, covered with seven cc. of concentrated nitric acid, and shortly after an equal amount of hydrochloric acid is added; after allowing these two acids to act at a temperature of about 60° C., seven grams of ammonium chloride are added and the solution is evaporated to dryness on a hot plate. Then remove from the hot plate and, on cooling slightly, add five cc. of ammonia water, twenty-five cc. of water, and fifteen cc. of bromine water, and boil for five minutes; filter the boiling hot solution through a fifteen-cm. filter, and wash three times with a boiling hot dilute solution of ammonium chloride. Collect the filtrate in a suitable beaker, acidify with dilute hydrochloric acid, add a piece of sheet aluminum, and boil to precipitate any copper and lead that may be present. So soon as these metals are precipitated, pour the hot solution through a filter, washing it with hot water. Acidify the solution, which should have a bulk of between 200 cc. and 400 cc.

The addition of ammonium chloride is to insure the complete solution of the zinc and to help the solution filter more rapidly. I do not use potassium chlorate, except in very minute quantities, and only when deemed absolutely necessary to decompose sulphides. In my own experience I find that the combination of the strong acids with ammonium chloride evolves some chlorine slowly, and I rarely find it necessary to use potassium

chlorate. The addition of ammonia water to the dry residue makes the iron precipitate less gelatinous, allowing the solution to filter rapidly.

The addition of bromine water can be omitted if manganese is known to be absent.

A portion of the cadmium that may be present is precipitated on the aluminum foil; should it be necessary to allow for the cadmium, another method must be used, as aluminum will not completely precipitate cadmium in the presence of ammonium salts if the amount of cadmium is large.

Cadmium is completely precipitated from hydrochloric and sulphuric acid solutions in the absence of ammonia salts.

**238. Titration.** The zinc solution should have a bulk of between 200 and 400 cc.; it should have an excess of not less than five cc. of concentrated hydrochloric acid and not more than ten cc. It should be heated to boiling, and the titration finished before it cools to 40° C.

A standard solution of potassium ferrocyanide is used with a dilute solution of uranium acetate as an indicator. About half of the hot solution is poured into a beaker, and the ferrocyanide run in from a burette until a drop removed with a rod colors the uranium solution brown. More of the reserved portion of the solution is then added and the titration brought to a close finally, by rinsing the beakers and finding the end point by proceeding slowly with the addition of the ferrocyanide solution.

**239. Standardizing.** Dissolve 22 grams of crystallized potassium ferrocyanide in a liter of water. Standardize by dissolving 0.2 gram of pure zinc in ten cc. of concentrated hydrochloric acid; dilute to 200 cc., add ten grams of ammonium chloride, heat to boiling, and titrate as described in section 238. Divide the weight of zinc taken

by the cc. of the solution required to find the value of one cc. It should be about 0.005 zinc.

In control and umpire work the amount of zinc used in standardizing should be approximately equal to the percentage of the zinc in the ore.

**240. Remarks.** This method has been used in my laboratory for several years past, and has been thoroughly tried out on all classes of ores, and it can be relied upon to give the true content of zinc in an ore.

In the "Journal of the American Chemical Society" for February, 1909, p. 205, will be found an article prepared by me entitled "A Study of the Ferrocyanide Method for the Determination of Zinc." The experience of the years since it was written have confirmed the results of that study, which called attention:

(1) To the absolute necessity of decomposing the potassium chlorate which may have been added.

(2) That lead should not be used to remove copper, when much copper is present.

(3) That aluminum will remove copper and lead, and when copper and lead are present, nearly all of any cadmium that might be present.

(4) That the aluminum salts do not affect the consumption of potassium ferrocyanide.

(5) That manganese, if present, must be removed.

(6) That when accurate work is required the conditions of standardizing should be nearly the conditions in titrating the ore.

The following is copied from A. H. Low's "Technical Methods of Ore Analysis," principally for the reason that the author feels that Mr. Low has contributed very much to the development of the volumetric method for zinc, and the results of his studies should always be considered by zinc analysts. My criticism of Low's method

is that the many separations and operations tend to give results below the true zinc content.

**241. Low's Method.** Prepare a solution of potassium ferrocyanide containing 22 grams of the crystallized salt in the liter. Standardize this solution as follows: Weigh carefully about 0.2 gram of pure zinc and dissolve in ten cc. of strong hydrochloric acid (sp.gr. 1.20), using a 400-cc. covered beaker. Dilute somewhat, place a piece of litmus paper in the solution as an indicator, and make faintly alkaline with ammonia. Again acidify faintly with hydrochloric acid, and then add three cc. excess of the strong acid. Dilute now to about 250 cc., and heat nearly to boiling. Titrate the hot liquid with the ferrocyanide solution as follows: Pour off about one-third of the zinc solution and set it aside in a beaker. Titrate the remainder by running in a few cubic centimeters at a time, until a drop, when tested on a porcelain plate with a drop of a five per cent solution of uranium nitrate, shows a brown tinge. Now add the greater part of the reserved portion and continue the titration more cautiously until the end point is again passed. Finally, add the last of the reserved portion, and then, to save rinsing out the beaker, pour a large part of the solution back into it again and then empty it once more. From this point finish the titration very carefully, ordinarily by testing after each addition of two drops. Instead of using a single drop of the zinc solution for the test, the reaction is sharper if a quantity equivalent to several drops be taken. If this is done only near the end of the titration the amount of zinc lost will be insignificant. A convenient way of making the test is to use a medicine dropper and place a single drop of the uranium solution in each depression of the test plate at the outset. By using a glass tube instead of a rod for a stirrer, any quantity of the solution

can quickly be removed for a test. When the final brown tinge is obtained, note the reading of the burette, and then wait a moment or two and observe if one or more of the preceding tests do not also develop a color. The end-point is always passed by a test or two, and the burette reading must be corrected accordingly. A further correction must also be made for the amount of ferrocyanide required to produce a color under the same conditions when no zinc is present. This is ordinarily two drops. One cc. of the standard solution will equal about 0.005 gram of zinc, or, in the case of ores, about one per cent, when 0.5 gram is taken for assay.

**242. Treatment of an Ore.** To 0.5 gram of the ore in a 200 cc. pear-shaped flask add 10 cc. of strong hydrochloric acid, and boil gently until the acid is perhaps half gone, then add 5 cc. of strong nitric acid, and continue the boiling to dryness. Again add 5 cc. of nitric acid and repeat the boiling nearly to dryness, so as to expel practically all the hydrochloric acid. Now add 10 cc. nitric acid, warm gently, if necessary, and see that all the salts are dissolved. If they fail to dissolve they will usually do so on the addition of a few drops of water. Finally add 5 grams of potassium chlorate and boil again. Manganese, if present, will be precipitated, but it may not all remain insoluble. Boil to complete dryness, but avoid overheating and fusing the residue. It is advisable to manipulate the flask in a holder over a free flame at this stage, to save time and avoid loss by bumping. Boiling may be conducted rapidly, and it is not necessary to expel every trace of liquid. The large excess of potassium salts serves simply as a diluent of the dry residue, and insures the completeness of the subsequent extraction of the zinc. When the flask and contents are sufficiently cool, add 35 cc. of a prepared ammoniacal solution



and heat to boiling. This solution is made by dissolving 200 grams of commercial ammonium chloride in a mixture of 500 cc. of strong ammonia water (sp.gr. 0.90) and 750 cc. of water. Boil the contents of the flask very gently (so as to avoid materially diminishing the bulk and also undue loss of ammonia) for a few minutes, or until the insoluble residue is completely disintegrated, and then add 15 cc. of strong bromine water, and continue the boiling for a short time. The bromine is to insure the complete precipitation of manganese; 15 cc. are usually sufficient, but when the ore contains much manganese, it is best to test the filtrate by boiling with more bromine water. Filter through a 9-cm. filter into a 400-cc. beaker.

Any ferric hydroxide present will usually appear of a fine granular nature, quite unlike the ordinary gelatinous precipitate. Incomplete drying at the end of the evaporation, or a partial fusion of the dry salt, are each likely to result in more or less of the ordinary ferric hydroxide that will retain some zinc. Wash out the flask with hot water, and then thoroughly wash the residue on the filter with a hot solution containing 100 grams of ammonium chloride and 50 cc. of strong ammonia to the liter.

Add a bit of litmus paper to the filtrate as an indicator, and then cautiously neutralize with strong hydrochloric acid, finally adding three cc. in excess.

Dilute the liquid with hot water to about 200 cc., heat to boiling, and add fifty cc. of strong hydrogen sulphide water. The mixture is now ready for titration. Titrate precisely as in the standardization.

If more convenient, or apparently advisable, pass a current of the gas through the nearly boiling solution diluted to 250 cc. Ordinarily the sulphide thus precipi-

tated need not be filtered off, as the discoloration produced by even ten per cent of copper, for instance, does not badly mask the uranium test. If the amount of copper is so large as to require filtration, it is necessary to work with a more acid solution to prevent any zinc from being carried down with the copper. In such a case use 10 cc. instead of 3 cc. Filter from the copper sulphide, washing with cold water, and to the filtrate add ammonia sufficient to neutralize 7 cc. HCl (as determined by a previous trial), thus leaving an excess of three cc. hydrochloric acid. Make up to about 250 cc.; heat nearly to boiling, and titrate the hot liquid with the standard ferrocyanide solution precisely as in the standardization. In correcting the final reading of the burette, it is usually sufficient to deduct for as many tests as show a brown tinge and one test additional. Multiply the number of cubic centimeters used by the percentage value of one cc. to obtain the per cent of zinc in the ore.

**243. Notes.** It is not sufficient to wash the iron residue, from which the zinc has been extracted, simply with hot water. An appreciable amount of zinc is likely to be retained unless the residue is thoroughly washed with the ammoniacal solution described. A direct test on a 40 per cent zinc ore showed a retention of 1.27 per cent which was afterwards easily washed out of the ammoniacal solution. The use of granulated lead as a precipitant of copper is not recommended. Lead acts more slowly than hydrogen sulphide, sometimes fails to entirely remove the copper, and always produces a solution with an unknown and variable acidity. Metallic aluminum (advocated by Headden, Furman, and others) is likewise unsuitable. The aluminum salts formed affect the titration and produce incorrect results.

Even when the zinc contents of a solution are approximately known, it is not advisable to omit pouring off a reserved portion and proceeding in the regular manner. The reaction between the ferrocyanide may be varied, at least temporarily, by varying the conditions, and a false end-point thus obtained by working too rapidly.

Cadmium is not completely precipitated by hydrogen sulphide from a slightly acid solution containing considerable alkali chloride. In the present method, therefore, cadmium is to a greater or less extent counted as zinc, small amounts not being precipitated at all by the hydrogen sulphide. Theoretically, one hundred parts cadmium equal 87.3 parts zinc.

Arsenic, when present in large amounts, may make trouble by retaining iron in the ammoniacal solution filtered from the residue. No attention need be paid to arsenic unless its presence in excess is thus indicated. In such a case, begin anew, and give the ore the following preliminary treatment: Evaporate the nitric acid solution of the ore, without adding potassium chlorate, nearly to dryness. Add five cc. of strong hydrochloric acid and boil it until it is half gone. Or, if the ore has been originally decomposed with hydrochloric acid, boil the mixture until only a few cc. remain, now add about two cc. of a solution of one gram of sulphur in five cc. of bromine, and boil nearly or quite to dryness, but avoid overheating. The arsenic will thus be sufficiently volatilized. Add, now, five cc. of strong nitric acid, and again boil to dryness to expel the hydrochloric acid. Finally, once more add nitric acid, and proceed in the usual manner as though just beginning with the ore. In case a large amount of free sulphur has been separated by the nitric acid treatment of the ore, it will be sufficient

to add the bromine alone instead of bromine and sulphur.

**244. Special Treatment for Oxidized Ores and Roasted Products.** Oxidized material will frequently fail to yield properly to a nitric acid treatment. In such cases it is better to begin with hydrochloric acid, since if the ore is not well decomposed there is no certainty that the zinc is all extracted.

Starting with 0.5 gram of ore in the flask as usual, add five cc. or more of strong hydrochloric acid. Roasted ores will generally yield gelatinous silica when treated with acid, and the mass is liable to cake and resist complete decomposition. With such material, first add a few cubic centimeters of water, and then add acid gradually, at the same time agitating the flask so that the mass cannot settle into a compact body, and agitate the mixture occasionally during the subsequent heating. Heat very gently, without boiling, until the oxidized matter has dissolved; then boil to pastiness and add six cc. of strong nitric acid. Boil, now, to complete dryness to expel all hydrochloric acid. To make sure that all of the hydrochloric acid is completely expelled it is best to treat this evaporation with nitric acid. If gelatinous silica was separated by the decomposition, take special pains to dehydrate it as thoroughly as possible at this point, but avoid overheating, which might cause it to partially recombine with the bases. After cooling, add ten cc. of nitric acid to the residue and proceed in the usual way.

**245. Treatment of Refractory Ores, etc.** No exact line of treatment can be prescribed for this class of material. It is sometimes best to extract and determine all the zinc possible in the usual way, and give a special treatment to the residue. If the undecomposed portion of the

residue is of a siliceous nature the following may suffice: Dissolve the ferric hydroxide, etc., on the filter in warm dilute hydrochloric acid. This will give a filtrate and a residue.

**246. Filtrate.** This may contain a little zinc. Heat nearly to boiling, add ammonia to excess, then bromine water, boil and filter, and wash with hot water. Acidify the filtrate with hydrochloric acid, and allow to boil and evaporate to a smaller bulk while proceeding with the residue.

**247. Residue.** Dry and ignite in a platinum dish to remove the filter paper, cool, add equal parts of hydrochloric and hydrofluoric acids, and digest on a water-bath until solution is complete, adding more acid if necessary, then evaporate to dryness. Take up in nitric acid, transfer to a 200-cc. flask, and continue by the regular method. When the solution in **246** has been boiled down to decompose chlorates, mix the two solutions. Finish in the regular manner, adding the zinc found to that previously determined. The insoluble portion of the residue may also be fused with alkali carbonate, the melt dissolved in hydrochloric acid, the solution transferred to a flask and treated as given above, the other operations being just as described.

Sometimes the ore itself may be treated at once with hydrochloric and hydrofluoric acids in a platinum dish, the residue after evaporation being then taken up in hydrochloric acid, the solution transferred to a flask, and the assay finished as previously described. Of course, silica will be practically all removed.

**248. Modification to Avoid Cadmium.** If it be desired to avoid the influence of cadmium, the regular method may be modified as follows: Begin by treating the ore in the usual way until the dry mass is obtained in the

flask ready for extraction. Add ten cc. of the prepared ammoniacal solution and ten cc. of water, and heat gently for a short time to effect a more or less complete disintegration, then add ten cc. of strong bromine water and twelve cc. of a solution of sodium hydroxide made by dissolving 200 grams in water and diluting to 500 cc. Boil until all odor of ammonia is expelled, then add twenty-five cc. of hot water, and filter through a 9-cm. filter. Wash first with a little hot water to obtain the chlorate solution, and finish the washing with hot sodium hydroxide solution of one-tenth the above strength. The cadmium is left in the residue. The decomposition of the chlorates and the balance of the assay are conducted in the usual manner. The result thus obtained is usually satisfactory. To test for zinc in the residue, place filter and contents in a beaker, and repeat the extractions with the alkaline solutions and the separation of the cadmium again as just described. If the final titration of this portion shows any zinc, it may be added to the amount already found.

The following method is apparently very accurate and well adapted to serve as a check on other methods in special cases. It requires considerably more time for its performance than the one just described, and is, perhaps, therefore, not so suitable for regular use in a busy technical laboratory.

**249. Waring's Method.\*** The method depends upon the separation of the zinc from manganese, iron, and aluminum by means of hydrogen sulphide, under slight pressure in a solution very slightly acidified by formic acid; the metals of the copper group have been previously separated by metallic iron or aluminum with simultaneous reduction of ferric salts. The operations are:

\* Low's Technical Methods of Ore Analysis (1909), p. 244.

**250.** (1) *Solution.* The calamine, willemite, franklinite, blende, and other soluble minerals, or ores containing them, are decomposed by hydrochloric acid or aqua regia, with subsequent treatment and evaporation with an excess of hydrochloric or sulphuric acid to thoroughly eliminate nitrous compounds. If zinc spinels or aluminates are present, the insoluble residue must be fused with a mixture of sodium carbonate and borax glass, the fused mass dissolved, and the solution added to the main one. If much silica is present, spinels are decomposed by fusion with sodium carbonate in a platinum crucible, any lead sulphate present having been extracted by ammonium acetate. In the absence of silica or boric acid, the spinels cannot be decomposed by fusion with sodium carbonate alone. In such a case they can be decomposed by prolonged fusion with an alkali bisulphate. Silicates, such as cinders from oxide furnaces, unchilled slags, and some natural silicates undecomposed by acids, must be fluxed or sintered with sodium carbonate before treatment with hydrochloric acid. It is not necessary, in any case, to evaporate to dryness to separate silica—it can be filtered off in the gelatinous state. This can be done very rapidly, after dilution with water, when the gelatinization has reached a maximum and before dehydration has begun. The gelatinous silica at this stage will not retain any traces of metals after a few washings.

**251.** (2) *Reduction.* To avoid the effect of reactions like



and at the same time to remove copper, silver, and bismuth before precipitating with hydrogen sulphide, the filtered solution, made fairly acid with hydrochloric

or sulphuric acid, is boiled for fifteen or twenty minutes with a strip of clean sheet iron or steel. By this treatment all the metals likely to be precipitated with zinc as sulphides are separated, except cadmium, which is not in the least degree reduced by metallic iron.

Mr. G. C. Stone has suggested the use of metallic aluminum for the reduction. This has the advantage of separating cadmium and lead along with other metals of the copper group, since both are completely precipitated by aluminum from a rather strongly acid boiling solution of sulphates or chlorides, so that when zinc only is to be determined, the subsequent operations are very much shortened.

Reduction may also be effected by means of sodium sulphite or thiosulphate, when copper, or copper and aluminum are to be determined from the same weighed portion.

The reduction is followed by filtration, the filtrate being received in a flask of about 300-cc. capacity.

**252. (3) *Neutralization.*** Add to the filtrate a drop of methyl orange, then run in, from a pipette, a rather dilute solution of sodium hydroxide, meanwhile constantly agitating the contents of the flask with a swirling motion, until the pink color barely, but permanently, changes to a light yellowish tint, and the cloudiness, due to the separation of hydroxides, fails to clear up entirely. Then add, drop by drop, enough 50-per cent formic acid (sp.gr. 1.12) to just restore the permanent pink color, and add up to half a cubic centimeter additional. Dilute the solution to 200 or 250 cc. (so that it will contain not more than 0.15 to 0.20 gram of metallic zinc in 100 cc.), and heat to about 80° C.

**253. (4) *Precipitation.*** A rubber stopper, through which passes the delivery tube from a source of supply



of hydrogen sulphide, is loosely placed in the neck of the flask, and a moderately rapid stream of gas allowed to pass through the hot liquid. When the precipitation of zinc sulphide is well under way, the stopper is pushed in tightly. Absorption of the gas ceases when all the zinc is precipitated; the precipitate settles quickly, and the gas pressure rises rapidly when the operation is completed. When several precipitations are to be made at the same time, the flasks are arranged in succession in the usual manner, and the first is removed when the precipitation is well started in the third, and so on, changing the gas connections as required. The outlet from the last flask is not closed until the precipitation is partially completed therein. Numerous experiments have shown that zinc can be completely precipitated and separated from the iron, manganese, and aluminum under the conditions named, by the passage of only a little more than the amount of hydrogen sulphide theoretically required. The use of a large excess is therefore unnecessary and is also undesirable.

254. (5) *Treatment of the Precipitate.* When the preceding operations have been properly performed, the precipitated zinc sulphide will be pure white, pulverulent, and very easily filtered off and washed. Hot water only need be used for washing; no zinc will dissolve or pass through the filter, as in the case of the slimy zinc hydro-sulphide precipitated from cold solutions in the usual manner. Pour the contents of the flask upon a filter at once, and wash with hot water. Spread the filter with its contents upon a large watch-glass, or on the inner wall of a capacious beaker, and wash the precipitate into the beaker by a jet of hot water. Wash the precipitating flask and the lower end of the gas delivery tube with ten cc. of strong hydrochloric acid, followed by hot

water, pouring the acid and washings successively over the washed filter onto the precipitate in the beaker. When the volume of the acid solution has reached 125 to 130 cc., the solution is warmed gently to dissolve the zinc sulphide completely. When cadmium is also present (i.e., when the reduction has been effected by metallic iron), the zinc sulphide will dissolve completely before any cadmium sulphide is dissolved. By practice and experience, the point when all the zinc is dissolved and only the brilliant cadmium sulphide remains can easily be distinguished. The solution is then further diluted with an equal volume of hydrogen sulphide water, allowed to settle, and the cadmium sulphide filtered off and estimated in the usual way by warming with acid ferric sulphate and titrating with permanganate. The iron equivalent of the permanganate used multiplied by 1.006 equals the cadmium. Properly performed, the result is accurate.

The solution of zinc sulphide in dilute hydrochloric acid is heated to 60° C. or more, made up to 200 to 250 cc. with hot water, a little ammonium chloride added, and it is ready for titration with ferrocyanide.

The method of separating zinc by hydrogen sulphide from nickel, cobalt, and manganese, recommended by Fresenius, is not applicable when iron is present, as iron is thrown down by hydrogen sulphide in the presence of sodium acetate.

**255. Modification for Low-grade Zinc Ores, Slags, Furnace Residues, etc.,** and for purposes wherein it is required to determine small amounts of zinc accurately.

Proceed exactly according to the method just described until the zinc sulphide precipitate has been washed, then, instead of dissolving the precipitate, dry and ignite it carefully in a clean muffle without separating it from

the paper. No loss of zinc will occur, nor will basic sulphate be formed, if the wet precipitate is ignited at the mouth of the muffle until the paper is consumed, and oxidation of the residue is then conducted at a low temperature (about  $450^{\circ}$ ) until at the last, when it may be moved back to where the temperature is near the melting-point of silver. As much as 0.15 gram of zinc sulphate can be completely oxidized in this way in forty to sixty minutes. The calcination may be effected in a smooth shallow scorifier an inch and a half in diameter, from which the calcined oxide can be brushed into the scale pan without appreciable loss. Calculate the zinc from the ZnO found by multiplying by 0.8035.

**256. Valuation.** In the Joplin district of Missouri, zinc ores are paid for on the basis of the selling price of spelter in St. Louis and the percentage of zinc in the ore. The price is found by taking the product of the price of the zinc per pound in St. Louis and the per cent of zinc in the ore and multiplying that by 16, and deducting from this amount \$10.50. For instance, when spelter is five cents a pound in St. Louis and the percentage of zinc in the ore is 50, the price per ton is  $(5 \times 50 \times 16) - \$10.50 = \$29.50$ . In Antwerp the formula used for finding the value in tons of 2000 pounds in U. S. currency would be: Deduct 8 from the percentage of zinc in the ore, multiply this figure by the price in London for spelter in cents (U. S.) per pound, multiplying this by 20, and deducting a figure, varying with the character of the ore market conditions, etc., averaging about \$15.00. From this formula a 50 per cent ore, when spelter in London is worth 5 cents per pound (U. S. currency), would bring \$27.00 a ton f.o.b. Antwerp.

In Mexico the zinc ores are usually paid for f.o.b. the cars at the mines at the rate of \$15.00 (U. S. currency)

per ton of 2000 pounds when the ore runs 40 per cent zinc, adding \$1.00 per ton for each additional per cent. Penalties are levied when the percentage of iron runs more than two per cent. Duties are for account of the shipper, when the U. S. government levies such duty on zinc ores going into the United States.

## PART II

### *NON-METALLIC DETERMINATIONS*

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#### CHAPTER XXIV

##### CHLORINE

It may be necessary to determine the amount of free chlorine in solution, as well as the amount of chlorine combined with hydrogen, or any of the metals.

**257. Free Chlorine.** A measured quantity of the solution is taken, from twenty-five to one hundred cc., as found convenient. An excess of an aqueous solution of potassium iodide is then added; the free chlorine decomposes the potassium iodide, the free iodine remaining in solution. The free iodine is then determined by titrating with a standardized solution of sodium thiosulphate, using a starch solution indicator, until the blue color due to the action of the free iodine on the starch paste disappears. The strength of the solution of sodium thiosulphate in iodine having been determined, its value in chlorine is found by multiplying the strength in iodine by 0.28. One atom of chlorine liberates one atom of iodine.

**258. Combined Chlorine.** With the exception of silver, lead, and mercurous chlorides, all of the metallic chlorides are soluble in water. If these salts are present, special means for their solution must be employed, and the methods

may be found in any of the standard works on quantitative analysis.\*

The chlorides, in weighed quantities of one-half, or one gram, are dissolved in water, and the solution made neutral, or at least only faintly acid with dilute acetic acid. The bulk of the solution should not be more than one hundred cc. One cc. of a two per cent solution of potassium chromate is then added, and a standard solution of silver nitrate is then run in from a burette until a permanent faint red tinge is formed, due to the formation of silver chromate. Stir the solution thoroughly after each addition of silver nitrate.

If free chlorine is present, the solution must be heated with sulphurous acid in excess to convert the chloride into hydrochloric acid, after which potassium chromate must be added to eliminate the excess of sulphurous acid. The solution is then made neutral, and when cooled, the total chlorine is determined by titrating as above with silver nitrate. The free chlorine found by the potassium iodide method must be determined and deducted from the total found, to obtain the combined chlorine.

The standard silver nitrate solution is made by dissolving 16.997 grams of the pure silver nitrate in one liter of water. One cc. of such a solution should equal 0.003545 gram of chlorine.

\* See p. 528, Vol. I, "Quantitative Chemical Analysis," Fresenius-Cohn.

## CHAPTER XXV

### PHOSPHORUS

In western smelter work determinations of phosphorus are seldom required. The following method will give good results under all conditions apt to arise except where the amounts of phosphorus are very small, as in the analysis of iron ores for the manufacture of steel. For such work it is best to use the methods described in "Blair's Iron and Steel Analysis."

**259. Decomposition.** Take half a gram of the pulp in a No. 7 casserole and treat with twenty cc. of strong hydrochloric acid, followed with ten cc. of strong nitric acid. After the ore is decomposed, using heat to complete the decomposition, dilute to one hundred cc. and filter; after washing the residue with hot water, neutralize the filtrate with ammonia water, when some of the iron may precipitate. Clear the filtrate with the addition of a few drops of nitric acid. Add ten grams of ammonium nitrate, and heat to about 70° C. To the hot solution add fifty cc. molybdate solution and digest at a temperature of between 60° and 70° C. for an hour; filter off any precipitate, and wash with cold water.

Test the filtrate for phosphoric acid by adding more molybdate solution and digesting as before. Should there be any further precipitate, filter it off and add the precipitate to the first.

Dissolve the precipitate on the filter with ammonia water and hot water, and wash the whole into a beaker, keeping the bulk below one hundred cc. Nearly neu-

tralize with hydrochloric acid, cool, and add magnesia mixture slowly, stirring vigorously after each drop, until there seems to be no precipitation. Wait fifteen minutes and then add twelve cc. of strong ammonia water. Allow to stand in a cool place for two hours; filter off the magnesium ammonium phosphate and wash it with a three per cent solution of ammonia until all chlorides are washed out. Then ignite in an annealing cup, starting at a low heat, until grayish white in color, then weigh as  $Mg_2P_2O_7$ . Calculate the  $P_2O_5$  by multiplying the weight by 0.27837, from which the percentage can be calculated.

**260. Molybdate Solution.** Dissolve one hundred grams of molybdic acid in 144 cc. of ammonia water, sp.gr. 0.9, and 271 cc. of water. Then slowly, with constant stirring, pour this solution into a mixture of 489 cc. of nitric acid (sp.gr. 1.42) and 1.148 cc. of water. Keep the mixture in a warm place for several days, decant the solution into a glass bottle, and hold for use.

**261. Magnesia Mixture.** Dissolve 22 grams of freshly ignited calcined magnesia in dilute hydrochloric acid, avoiding an excess of acid. Then add excess of the magnesia and boil for a few minutes to precipitate iron, alumina, and any phosphoric acid that might be in the magnesia, then filter, and add 280 grams ammonium chloride, 261 cc. of ammonia water, and water enough to make the bulk 2000 cc.

Instead of magnesia, 110 grams of crystallized magnesium chloride may be dissolved in water as above.

**262. Volumetric Method.\*** This method is based upon first separating the phosphoric acid from other substances by precipitating as magnesium phosphate (259); then

\* Adapted from Beringer's Text Book of Assaying.



dissolving the latter and titrating with a standard solution of uranium acetate. If arsenic is a constituent of the material, it must first of all be removed as the sulphide by precipitation with hydrogen sulphide (29).

**263. Preparation of the Solution.** The magnesium phosphate after being filtered off and washed (259), is dissolved in a small quantity of dilute hydrochloric acid, and ammonia added till just alkaline; then three grams of sodium acetate and just enough acetic acid to make the solution feebly acid, are added. The solution is then diluted to 150 cc. and heated to boiling.

**264. Titration.** When boiling hot, run in the same standard solution of uranium acetate used for arsenic (35) to end reaction, with an indicator solution of potassium ferrocyanide.

**265. Standardizing.** Dissolve 0.2 gram of clear transparent crystals of hydrogen disodium phosphate,  $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , in water, add three grams of sodium acetate and two drops of dilute acetic acid, heat to boiling, and titrate to end reaction. 0.2 multiplied by 0.2751, and this quantity divided by the cc. of uranium acetate used, will give the strength of one cc. in  $\text{P}_2\text{O}_5$ . The strength may be calculated from the As strength by multiplying the As value by 0.9466.

**266. Remarks.** The chemistry of the reactions involved are similar to those with arsenic (37), and the influence of foreign substances is nearly identical.

## CHAPTER XXVI

### SELENIUM AND TELLURIUM

It is not often that the technical chemist is called upon for the determination of these non-metallic elements.

**267. Detection.** The best test for *selenium* is to heat it on charcoal in a good oxidizing flame, when a white incrustation will be formed on the coal. On moistening this with a solution of stannous chloride it becomes red, owing to the separation of metallic selenium.

*Tellurium* is best tested for by placing a small portion of the finely powdered substance in a casserole, covering with strong sulphuric acid and warming gently for about five minutes; a purple or carmine tint indicates the presence of tellurium.

**268. Determination.** A half gram, or more, of the finely divided pulp is treated with 25 cc. of aqua regia in a No. 2 casserole until decomposed. Water is then added, and the solution filtered off. The gold is then precipitated by adding half a gram of oxalic acid and allowing to stand for a short while. The liquid is clarified by filtration and treated with fifteen cc. of a strong solution of sulphurous acid, which will precipitate all selenium and tellurium. The precipitate is filtered off and transferred to a casserole, and then treated with dilute nitric acid, which dissolves the selenium. The tellurous oxide is filtered off, using a tared filter, then dried and weighed. The weight of  $\text{TeO}_2$  is multiplied by 0.802 to obtain the weight of tellurium.

The solution from the tellurous oxide is then treated with fifteen cc. of a strong solution of sulphurous acid to precipitate the selenium as selenious oxide. It is filtered off through a tared filter, dried, and weighed. The weight of  $\text{SeO}_2$  multiplied by 0.7826 will give the weight of selenium.

## CHAPTER XVII

### SILICA

**269. Insoluble Residue.** This is an indefinite determination, and may be defined as that portion of an ore that fails to go into solution after treatment with hydrochloric and nitric acids with subsequent evaporation to dryness, then treating again with hydrochloric acid, diluting with water, filtering and washing with hot water, followed by washing with a hot solution of ammonium chloride to remove lead sulphate (if present) and a washing with ammonia to remove silver chloride.

The residue remaining after such treatment is then ignited and weighed and called "insoluble" or "silica."

If barium sulphate is present it will be counted as "insoluble" but when this is known the barium sulphate is determined and the amount deducted from the "insoluble" found.

Different ores require slightly varied treatments, consequently it seldom happens that different chemists secure the same results on the same pulp.

The following method is the one followed in my work. All that I can say is—it is no more faulty than any other method known to me.

**270. Decomposition.** One-half a gram of ore is weighed out into a casserole, covered with five cc. of concentrated hydrochloric acid, and allowed to stand for at least ten minutes at room temperature, when an equal quantity of strong nitric acid is added, and the assay kept for from fifteen to thirty minutes at a temperature of near 60° C.

Then the solution is evaporated to dryness on a hot plate, the casserole being kept covered with a watch-glass. It is removed from the hot plate and moistened with strong hydrochloric acid while still warm.

Water is then added, the whole heated, and filtered while hot. Everything in the casserole is carefully washed into the filter, and all iron washed out with boiling water. If lead is present, a hot boiling solution of ammonium chloride should be used for one or two washings; and if much silver is present in the ore, the residue should be washed once with ammonia water, after which it is ignited in an annealing cup in the muffle and then weighed.

**271. Presence of Barium Salts.** When barium salts are known to be present, the residue, after weighing, is fused in a platinum crucible with sodium and potassium carbonates, and the barium determined as in section 47; the amount of barium sulphate thus found is deducted from the insoluble residue.

**272. True Silica.** The residue from the acid treatment is ignited in a platinum crucible and is then mixed with five grams of chemically pure dry sodium carbonate and fused in a blast lamp, keeping the cover on the crucible. On cooling, put the crucible in a porcelain dish of suitable size, cover with water, and heat to boiling; add cautiously from time to time dilute hydrochloric acid. As soon as the crucible is cleaned remove it and evaporate the solution to dryness on a hot plate. Care must be taken to prevent loss by spattering, and all lumps should be broken down by pressure with a glass rod to insure making all silica insoluble. Then moisten thoroughly with hydrochloric acid, warm, and add one hundred cc. of water, heat to boiling, and filter. Care must be taken in washing with hot water to remove all sodium salts. This being accomplished, ignite in a platinum crucible,

and weigh when cooled. It is pure  $\text{SiO}_2$ , unless barium sulphate is present in the ore. It will then be necessary to add hydrofluoric acid to the residue in the crucible and evaporate it cautiously to dryness, finally heating over a free flame. Repeat this operation several times, when all the silica will be volatilized, and if no barium be present there will be no residue. The residue remaining after treatment with hydrofluoric acid is deducted from the silica found.

#### SMEILTER METHODS \*

**273.** The following are the methods used in the plants of the American Smelting and Refining Co.:

Unless there is some special reason otherwise, one-half a gram is taken in all cases for determination.

**274. Sulphides.** Treat in a No. 10 beaker, or small casserole, with seven to ten cc. strong nitric acid. Heat gently until strong action has ceased. Evaporate to dryness and bake until free from acid. Cool, add about twenty cc. hydrochloric acid (one part water to one part acid), and heat until solution is as complete as possible. Filter, and wash, first with hot dilute hydrochloric acid, then hot water. Ignite and weigh.

Occasionally some ores high in zinc and lead sulphides may be treated to advantage first with hydrochloric acid, then following as above, but the results should be the same in either case if properly carried out.

**275. Oxidized Ores in General.** Treat with seven to ten cc. strong hydrochloric acid. Boil until dissolved; add a little nitric acid (one-half a cc. is usually plenty), evaporate to dryness, and bake to the complete expulsion

\* Western Chemist and Metallurgist, Vol. III, pp. 120, 121.

of acid fumes. Cool, take up with hydrochloric acid, and proceed as with sulphides.

Leadville manganese ores are not treated with nitric acid.

**276. Leady Oxide Ores.** Some of these, such as Midas and Percy La Salle, usually yield gelatinous silica, and must be carefully dehydrated at not too high a temperature.

**277. Oxidized Material which has been Strongly Ignited.** This covers such products as Cripple Creek concentrates. Digest with hydrochloric acid, without boiling at first, then evaporate nearly to dryness, add a few drops of nitric acid, and evaporate to complete dryness. Occasionally it may be necessary to repeat this treatment, which is a matter of individual judgment. Finally bake to complete expulsion of acid and proceed as before.

**278. Roasted Ores, Acid Works Residues, etc.** Digest with hydrochloric acid, without boiling, until oxidized portion is dissolved, add three cc. of nitric acid, boil to decompose sulphides, evaporate to dryness, and proceed as before.

**279. Ores or Product Containing Magnetite.** Some mixed oxidized and sulphide ores, such as the Ibex, and other Leadville ores, and often furnace mattes, contain magnetite. When this is known or suspected, the material is treated as above under "Roasted Ores, etc.," except that nitric acid in larger quantities may sometimes be necessary.

**280. Barium Sulphate Ores.** Treat with ten cc. hydrochloric acid (1 part acid and 1 part water), boiling a few minutes, add three to five cc. nitric acid, and after action has ceased evaporate to dryness, bake, and proceed as usual.

After total insoluble is weighed, fuse with sodium

carbonate or mixed carbonates, digest the melt with water until disintegrated, filter, and wash. Wash out the fusion crucible with three to five cc. hydrochloric acid (1:1), and with this dissolve the residue on the filter, being careful that all the residue is all dissolved and the filter washed clean. Precipitate the barium in boiling solution with a slight excess of dilute sulphuric acid, and allow to stand at least two hours before filtering. The barium sulphate so obtained is deducted from the total insoluble to give the insoluble residue.

**281. General Notes.** Care must be taken to insure the removal of all lead salts from the insoluble residue. Filtrations should be conducted rapidly and with hot solutions, in which case washing with hot dilute hydrochloric acid is perfectly safe. However, washing with hot ammonium chloride or acetate solution is often used, and has no objections. This removal of lead needs special care in barium sulphate ores, as this latter seems to render the complete solution of the lead salts more difficult. The use of the Baker & Adamson No. A filter paper is recommended as less likely than most papers to allow fine precipitates to pass through.

**282. Remarks.** There are so many unknown factors in determinations of "insoluble residue" that cause varying, sometimes highly differing, results that cannot always be settled according to their merits. It is devoutly to be hoped that the smelters will, at no distant day, arrange their ore schedules so that this determination may be abolished and a true "silica" or "fused silica" be substituted.

**283. Valuation.** The presence of silica in ores is detrimental, and the smelters usually penalize it at the rate of ten cents per unit.



## CHAPTER XXVIII

### SULPHUR

**284. Detection.** Fuse a portion of the substance on platinum foil with dry sodium carbonate, free from sulphur, using the reducing flame of a blowpipe. Place a portion of the fused mass on a clean silver coin and moisten with water. The formation of a brown, or black, stain on the coin, due to the formation of silver sulphide, is a good test for the presence of sulphur.

Sulphur is determined gravimetrically by converting it into sulphuric acid, or soluble sulphates, and precipitating it with barium chloride.

**285. Decomposition.** One-half gram of the ore is placed in a casserole and treated with ten cc. of strong nitric acid. Use gentle heat and employ potassium chlorate cautiously, as necessary, to oxidize all sulphur. Then evaporate to dryness and add five cc. of strong hydrochloric acid. Evaporate to dryness a second time, add five cc. of strong hydrochloric acid, and dilute with water to about 100 cc. and filter off. Wash the residue with a boiling hot solution of ammonium chloride and dissolve any lead sulphate. Heat the filtrate to boiling, add ammonia to excess, and filter off the precipitated hydroxides, while the solution is still hot. Make the filtrate slightly acid with hydrochloric acid, then add an excess of five cc. of concentrated hydrochloric acid. At this stage of the operation the solution should have a bulk of about 300 cc.

**286. Precipitation.** Heat to boiling and add slowly a hot solution of barium chloride until in excess. Allow to stand in a hot place for several hours, and filter while hot, washing the precipitate with hot water. The moist precipitate and filter is transferred to an annealing cup and burned in an open muffle till white. The residue, which should be perfectly white, is dusted out on the scale pan; and the weight of sulphur determined by multiplying by 0.1373, when the percentage is quickly calculated.

**287. Modification for Barium Sulphate.** Treat as described in section 285. Ignite the insoluble residue in a platinum crucible, add four times its bulk of sodium carbonate and fuse. Cool, and take up the fusion with water, and after filtering and washing with hot water, make the filtrate acid with hydrochloric acid and mix this solution with the filtrate obtained in the preliminary treatment, and proceed as in section 286.

**288. Volumetric Method.\*** Take half a gram, or more, of the material and fuse it in a platinum crucible with ten grams of a mixture of equal parts of sodium carbonate and potassium nitrate, both free from sulphur. After fusion is complete, cool, place the crucible and its contents in a No. 3 casserole, and boil with water until all of the melt is extracted; filter, wash with boiling water, and reserve the filtrate for the determination.

**289. Titration.** Add five grams of sodium acetate to the solution, acidify by adding two cc. of glacial acetic acid, and heat to boiling. Run into the hot solution a standard solution of barium chloride until a drop gives a pale yellow precipitate on the spot plate with a solution of potassium chromate. The spot plate should have a dark ground, and a piece of glass laid upon a sheet of black

\* Adapted from Beringer's "Text Book of Assaying."

paper makes a satisfactory article. A portion of the solution should be reserved, and the standard run in to a strong end reaction, after which the reserve may be added and the final end-point more accurately determined by allowing the precipitate to subside partly before withdrawing the drop.

**290. Standardizing.** The standard solution is made by dissolving 36.25 grams of crystallized barium chloride in a liter of water; if the pure compound is used each cc. will correspond to 0.005 gram of sulphur. If it is deemed essential to standardize, dissolve any soluble sulphate in water and treat as in (289). The indicator solution is made by dissolving one gram of potassium chromate in one hundred cc. of water.

**291. Remarks.** If the material treated is a strong sulphide, loss is apt to occur in the fusion, and it will be best to employ Ebaugh and Sprague's method for decomposition (28), which has been recommended for the decomposition of sulphides as well as for arsenides.

If a better indicator could be found this would make a satisfactory method.

Sulphur is usually detrimental to smelting ores, and a charge of twenty-five cents is made for each per cent of sulphur up to a maximum charge of \$4.50 per ton.

## PART III

### MISCELLANEOUS

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#### CHAPTER XXIX

##### CEMENTS \*

Weigh out two grams of the finely powdered material in a No. 2 casserole and treat with fifteen cc. of concentrated hydrochloric acid, seven cc. of concentrated nitric acid, and finally evaporate to dryness. Take up with ten cc. of hydrochloric acid, add fifty cc. of water, filter off into a 250-cc. graduated flask.

The residue is ignited and fused in a platinum crucible with sodium carbonate, extracted with water and evaporated to dryness as in section 278. The silica is ignited and weighed as such; and the filtrate from the silica is treated with ammonia water and the aluminum precipitate is filtered off, ignited, and weighed as  $\text{Al}_2\text{O}_3$ .

Take 100 cc. of the solution and make alkaline with ammonia, then filter, and wash. The residue, which is composed of iron and aluminum sesquioxides, is filtered off; the filtrate is heated to boiling and the lime precipitated with ammonium oxalate, filtered off, and determined gravimetrically or by the permanganate method.

\* Adapted from Stillman's "Engineering Chemistry."

The filtrate from the lime is evaporated to dryness in a platinum dish and the ammonium salts driven off by ignition, the residue cooled, treated with 50 cc. of water and filtered off. The residue is  $\text{MgO}$ , which is ignited and weighed as such. The filtrate from it also contains some magnesium as well as the potassium and sodium. A few drops of sulphuric acid are added to this filtrate and it is then evaporated to dryness in a small platinum dish; the increased weight represents the sulphates of these bases. It is taken up with water, mixed well, and divided into two equal parts. In one part the  $\text{MgO}$  is determined by precipitation as  $\text{Mg}_2\text{P}_2\text{O}_7$ , as in section 168. To the other portion platinum chloride is added in excess with a few drops of hydrochloric acid, and the whole evaporated to dryness on the water bath. It is filtered after moistening with alcohol and the potassium determined, as in section 209.

The magnesium and the potassium found are calculated as sulphates, and this subtracted from the weight of the magnesium, potassium, and sodium sulphates gives the weight of sodium sulphate, from which the  $\text{Na}_2\text{O}$  can be calculated.

The residue of iron and alumina is taken up with hydrochloric acid, and an excess of sodium peroxide is added; the iron sesquioxide is filtered off, washed well with hot water, ignited, and weighed as  $\text{Fe}_2\text{O}_3$ .

The filtrate is acidified with hydrochloric acid, ammonia added, and the alumina filtered off; this is washed well, ignited, and weighed as  $\text{Al}_2\text{O}_3$ .

Fifty cc. of the solution are taken for the determination of sulphuric oxide by precipitation with barium chloride, as in section 286.

Cement frequently contains small percentages of carbonic acid.

In addition to the chemical analysis, certain physical tests are also required to determine the value of the cements. These methods are foreign to the plan of this book, and recourse should be had to the book "Portland Cements," by D. B. Butler.

## CHAPTER XXX

### CLAYS \*

Clays or sands to be used in the manufacture of fire-brick, retorts, etc., should contain only small amounts of the alkalies and iron. The maximum amount of sodium and potassium is only one per cent, while the maximum amount of iron oxide is two per cent.

The clay must be thoroughly air dried and then finely ground. The following determinations will be required, for a complete analysis:

**292. Total Silica.** One gram is fused with ten grams of an equal mixture of sodium and potassium carbonates in a large platinum crucible. The fusion must be complete, and the mass kept at a red heat for at least thirty minutes. Allow to cool, treat with an excess of boiling water, make acid with hydrochloric acid, and evaporate to dryness. Take up with twenty-five cc. of hydrochloric acid, add water, boil, and filter through an ashless filter. Wash well with boiling water, dry, ignite, and weigh as "silica (total)."

**293. Hydrated Silica.** Boil four grams of the powdered clay with a strong solution of sodium carbonate in a platinum dish for a period of ten hours, then filter, and wash well with hot water. Acidify the filtrate with hydrochloric acid and evaporate to dryness; take up with a few cc. of hydrochloric acid, then add hot water, filter,

\* Adapted from Stillman's "Engineering Chemistry "

wash, dry, ignite, and weigh as  $\text{SiO}_2$ , and report it as "hydrated silica."

**294. Quartz Sand.** Treat two grams of the powdered clay with a mixture of equal parts of sulphuric acid and water for a period of eight hours; then evaporate to dryness, cool, add water and filter off the undissolved residue which wash, dry, ignite, and weigh. This residue contains all of the silica in the clay and all silicates not decomposed by acids; its percentage is calculated.

A boiling hot solution of sodium carbonate in a platinum dish is made ready, and the last residue is gradually added to it and boiled for an hour; then decant the solution through a filter, and add a fresh amount of sodium carbonate solution and repeat the operation again and again, until a few drops of the fluid remain clear on the addition of a little ammonium chloride. Then transfer the residue to the filter and wash it first with dilute hydrochloric acid, finally with hot water, dry, ignite, and weigh, and calculate the percentage as "quartz sand."

**295. Combined Silica.** The percentage of "quartz sand" is added to the percentage of "hydrated silica" and the result deducted from the per cent of the residue left by the sulphuric acid treatment in section 294 to find the percentage of "combined silica."

If the percentage of "total silica" found by fusion be less than the sum of the percentages of quartz, sand, combined silica, and hydrated silica, the difference is due to silicates in the quartz.

**296. Potassium and Sodium.** One gram of the dried clay is placed in a small platinum dish and treated with ten cc. of sulphuric acid and twenty cc. of hydrofluoric acid, and gently heated to volatilize the silica; the operation is repeated until all of the silica is volatilized, and then



the excess of acid is driven off. Allow to cool, add twenty cc. of warm hydrochloric acid, then twenty-five cc. of water, and transfer the contents of the platinum dish to a No. 3 beaker, add two cc. of nitric acid, then add ammonia in excess, boil, and filter off the ferric oxide and alumina. The residue is set aside and the alumina determined as in section 5.

The calcium in the filtrate is precipitated with ammonium oxalate and filtered off; after which the magnesium is precipitated with ammonium phosphate; the filtrate from the magnesium is evaporated to dryness in a platinum dish and ignited to drive off all ammonium salts. The residue is treated with hydrochloric acid, and the potassium precipitated with platinic chloride as  $K_2PtCl_6$ , filtered off, and weighed after washing on a tared filter. The washings and filtrate from this precipitate are evaporated to dryness, and the residue heated with oxalic acid to decompose the platinum compounds; water is then added together with a few drops of sulphuric acid, and the whole evaporated to dryness, previously filtering off the platinum residue. The last residue is weighed as  $Na_2SO_4$ , from which  $Na_2O$  is calculated.

**297. Iron, Calcium, etc.** The filtrate from the fusion with carbonates of sodium and potassium, section 292, is made nearly alkaline with sodium carbonate, sodium acetate added, and then boiled hard to precipitate the iron and aluminum hydroxides. Filter off the precipitate, wash and redissolve it in hydrochloric acid, and determine the iron by titration with permanganate, or potassium dichromate. The filtrate from the iron is set aside in a warm place, twenty cc. of bromine water are added, and allowed to stand for an hour, when it is boiled, and the manganese precipitated is filtered off and weighed as  $Mn_3O_4$ , from which is calculated the percentage of  $MnO_2$ .

The filtrate from the manganese is treated with ammonium oxalate to precipitate the calcium, which is filtered off and the calcium determined volumetrically, as in section 75, or it is dried and weighed, after strong ignition as  $\text{CaO}$ .

The magnesium is determined in the filtrate from the calcium by precipitating with sodium phosphate; after the magnesium phosphate is filtered off, it is dried, ignited, and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$ , from which the  $\text{MgO}$  is calculated.

**298. Sulphur Trioxide.** This is determined by fusing one gram with sodium and potassium carbonates, separating the silica as usual, taking up with hydrochloric acid, and precipitating the sulphur trioxide with a solution of barium chloride and weighing as  $\text{BaSO}_4$ .

**299. Titanic Oxide.** Fuse five grams of the clay with an excess of a mixture of equal parts of sodium fluoride and sodium bisulphate in a platinum crucible for thirty minutes at a red heat. Cool, and treat the mass with water, adding about two hundred cc., then add potassium hydroxide in excess, and filter off the impure titanic oxide, wash, dry, ignite, and fuse with twelve times its weight of sodium bisulphate; allow to cool, and treat with concentrated sulphuric acid. This is then poured into six hundred cc. of water, boiled for an hour, and the precipitated titanic oxide filtered off, washed, dried, ignited, and weighed as  $\text{TiO}_2$ .

**300. Water of Hydration.** Heat two grams of the clay in a platinum crucible in the flame of a gas lamp until there is no further loss of weight. The loss of weight is calculated as combined water.

## CHAPTER XXXI

### COAL AND COKE

The determinations usually made of these substances are for moisture, volatile combustible matter, fixed carbon, ash, phosphorus, and sulphur. The conventional method, and the one generally employed, is that recommended by the American Chemical Society.

The sample is first coarsely ground, and a sample is immediately cut out for the moisture determination; the remainder is ground to pass one hundred mesh, and kept in a tightly stoppered bottle for use in the other determinations.

**301. Moisture.** Weigh out one gram into a weighed porcelain or platinum crucible, and dry at a temperature of 104–107° C. until the weight is constant. The loss in weight is calculated as moisture.

**302. Volatile Combustible Matter.** Place in a weighed platinum crucible one gram of the undried powdered coal, using a tightly fitting cover for the crucible. Heat over a full clear flame for seven minutes, by which time the smoke fumes should have ceased to come off and the upper surface of the lid should be clean. Cool and weigh. The loss in weight, less the amount of determined moisture, is the "volatile combustible matter." The remainder is coke.

**303. Fixed Carbon and Ash.** Burn the portion used for the determination of moisture with the crucible open until it is white, grayish, and free from carbon. Start with a moderate heat, increasing it gradually. A plati-

num crucible should be used. The weight of the burned residue is the "ash," and the fixed carbon is the weight of the residue after driving off the volatile matter, less the weight of the ash.

**304. Sulphur.** Eschka's method is as follows: One gram of the finely powdered coal is weighed into a large platinum dish, or crucible, of about one hundred cc. capacity. A mixture of one part of dry sodium carbonate and two parts of magnesia is made, and a gram and a half of the mixture is mixed thoroughly with the powdered coal. Heat gradually to low redness, stirring with a platinum rod until all of the carbon is burned off; cool, and rinse out the residue into a beaker, making the bulk about fifty cc. Then add fifteen cc. of bromine water and boil for five minutes. Decant through a filter, and boil the residue twice with thirty cc. of water each time, and transfer the residue to the filter and wash until all of the soluble matter is washed out of the residue. ✓ Add two cc. of strong hydrochloric acid and boil until all of the bromine is expelled. Then add ten cc. of a ten per cent solution of barium chloride, adding it drop by drop with constant stirring. Allow to stand in a warm place until it settles clear, then filter off the barium sulphate, washing it thoroughly with hot water. Transfer to an annealing cup and ignite in the muffle, cool, and weigh the  $\text{BaSO}_4$ . Multiply this weight by 0.1373 to obtain the weight of sulphur. The reagents employed must be free from sulphur.

**305. Phosphorus.** Weigh out five grams of the coarsely crushed coal, or coke, into a platinum dish, and burn off the carbonaceous matter, best in a hot muffle. Transfer the residue to a casserole, or beaker, and digest with hydrochloric acid for from fifteen to thirty minutes, filter into a casserole, and after washing the residue on the

filter, evaporate to dryness on the hot plate. Cover the residue in the casserole with twenty-five cc. of strong nitric acid and boil until the bulk is reduced one-half, then add twelve cc. of water, and filter, receiving the filtrate in a 200-cc. flask; wash well with water. The total volume should not exceed fifty cc. Heat to 40° C., and add sixty cc. of molybdate solution, stopper the flask, and shake for fifteen minutes. Then filter through a 7-cm. washed filter previously dried at 110° C. and weighed. Wash with a two per cent solution of nitric acid and then twice with ninety-five per cent alcohol. Dry at 110° C. and weigh. Multiply the weight of the precipitate by 0.0163 to obtain the weight of phosphorus.

The molybdate solution is prepared by mixing 100 grams of molybdic acid with 265 cc. of water, adding 155 cc. of strong ammonia water, and stirring until solution is accomplished. Then add 60 cc. of concentrated nitric acid, stir well, and pour into a mixture of 395 cc. of strong nitric acid with 1,100 cc. of distilled water, stirring constantly. Allow to stand for twenty-four hours before using it.

## CHAPTER XXXII

### SLAG ANALYSIS

The determinations in a slag may include silica, iron, alumina, zinc, calcium, magnesium, potassium, sodium, copper, lead, manganese, sulphur, and phosphoric acid; also gold and silver.

**306. Decomposition.** If the slags have been chilled, it is probable that they will decompose with simple acid treatment, in which event start with two grams of the powdered slag. If they will not decompose with acid treatment, it will be necessary to fuse two grams with sodium and potassium carbonates. Both treatments are described fully under silica, and the reader will refer to that chapter for instructions in detail. In either case the filtrate from the silica is caught in a 250-cc. graduated flask, and after thorough washing, the flask is filled up to the mark with water and thoroughly mixed.

**307. Phosphoric Acid.** Take fifty cc. of the solution and treat as in section 259.

**308. Sulphur.** Take fifty cc. of the solution and precipitate with barium chloride, as in section 286.

**309. Iron.** Take fifty cc. for the determination of iron, reduce, and titrate with permanganate, or dichromate solution, as in sections 141, 143.

**310. Alumina, etc.** Take fifty cc. of the solution and add an excess of ammonia water and filter off the precipitated hydroxides. Wash the precipitate after filtering with hot water, saving the filtrate for the determination of calcium with ammonium oxalate, as in section 74, and

the magnesium, as in section 168. The hydroxide precipitate is taken up with hydrochloric acid and the alumina determined, as in section 5.

**311. Manganese.** Another fifty cc. is made nearly alkaline with sodium carbonate, ten grams of sodium acetate are added, and the solution is boiled to precipitate the iron and alumina. The filtrate is treated with fifteen cc. of bromine water and made alkaline with ammonia water, and after boiling, the manganese is filtered off, washed, and ignited and weighed as  $Mn_3O_4$ , from which the  $MnO$  is calculated.

**312. Lead, Zinc, and Copper** are determined by taking from one to two grams of the pulp and determining these constituents according to the volumetric methods described under their respective chapters.

In reporting the results of a slag analysis, the constituents found are reported as  $SiO_2$ ,  $P_2O_5$ , S,  $Al_2O_3$ ,  $CaO$ ,  $MgO$ ,  $FeO$ ,  $MnO$ ,  $PbO$ ,  $ZnO$ ,  $CuO$ , Ag, and Au.

## CHAPTER XXXIII

### WATER

The following method is for the analysis of waters for boiler use only.

Evaporate one liter of the water in a platinum dish to dryness, finishing at a temperature not to exceed  $105^{\circ}\text{C}$ ., cool, and weigh total solids. Then ignite slowly at a dull red heat, cool again and weigh. The loss is volatile matter and carbonaceous matter. Pour ten cc. of concentrated hydrochloric acid over the residue in the dish and warm gently; then add twenty-five cc. of water, boil, and filter into graduated flask, wash well and fill up to the mark and after mixing well divide into two equal parts. Keep the bulk down as far as possible.

**313. Residue.** The matter on the filter consists of silica, with possible aluminum silicate and calcium sulphate. Ignite it in platinum crucible and weigh. It may be reported as "insoluble." Or fuse with dry sodium carbonate in a platinum crucible, dissolve the fused mass in water and hydrochloric acid and evaporate to dryness. Treat with hydrochloric acid and water and filter. Wash well, and ignite the filter, reporting the weight as  $\text{SiO}_2$ .

Make the filtrate alkaline with ammonia, filter off any aluminum and iron oxides, ignite, and weigh it as such. The calcium in this filtrate may be precipitated with ammonium oxalate, filtered off, ignited, and weighed as  $\text{CaO}$ .

**314. Filtrate from First Residue.** Take one-fourth of



this filtrate and determine the  $\text{SO}_3$  by precipitation with barium chloride. Multiply the result by four. Make the other three-fourths alkaline with ammonia, boil, and filter off any precipitate, which is ignited and weighed as  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ ; multiply the result by four and divide by three.

To the filtrate from the iron and aluminum add ammonium oxalate, following usual details, filter, wash, and weigh as  $\text{CaO}$ . Multiply the result by four and divide by three.

The filtrate from the calcium oxalate is divided into two equal portions. In one portion the magnesium is determined by precipitation with sodium phosphate and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$ . Calculate the  $\text{MgO}$  found in it as  $\text{MgSO}_4$ .

The other portion of the filtrate is evaporated with the addition of sulphuric acid, and ignited to constant weight. The residue is  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4$ . The weight of  $\text{MgSO}_4$  previously found is deducted from the weight, and the remainder calculated as  $\text{Na}_2\text{O}$ . Multiply this by eight and divide by three to give the weight of  $\text{Na}_2\text{O}$  in the water. There is no need to determine the  $\text{K}_2\text{O}$ ; this may exist, but it is safe to call all the alkalies  $\text{Na}_2\text{O}$ .

**315. Chlorine.** This is determined by concentrating 250 cc. of the water to a small bulk and determining it as in section 258. Multiply the result by four.

**316. Carbonic Acid.** Combine all the chlorine found with alkalies and the sulphuric acid with any remaining portion, and then with the  $\text{CaO}$  and  $\text{MgO}$ . The amount of  $\text{CO}_2$  necessary to convert any remaining  $\text{MgO}$  and  $\text{CaO}$  is then calculated, and in this way the  $\text{CO}_2$  combined is determined.

**317. Remarks.** If the water is not clear it should be filtered. The results of analysis are reported:

1. Suspended matter.
2. Incrusting solids, comprising: Silica,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{MgCO}_3$ ,  $\text{MgSO}_4$ , and  $\text{MgCl}_2$ .
3. Non-incrusting solids, comprising:  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ , and organic matter.

The results are reported in fractions of a gram per liter. To convert milligrams per liter into grams per imperial gallon, multiply the number of milligrams by 0.07; to convert milligrams per liter into grams per U. S. gallon, multiply by 0.0583.

## CHAPTER XXXIV

### METHODS OF ASSAYING IN CYANIDE PLANTS

In addition to the ordinary fire assays for silver and gold, the assayer of a cyanide plant is called upon to determine the alkalinity of the solutions; the consumption of alkali by the ores; the strength of the solutions in potassium cyanide, at various stages of the operations; and the amounts of silver and gold held by the solutions.

**318. Alkalinity.** A standard solution of sulphuric acid is made so that one cc. of it will equal one cc. of a solution of sodium hydroxide with 0.04 gram of NaOH to the cc. This is accomplished by dissolving 30 cc. of concentrated sulphuric acid in a measured amount of water, say, 900 cc., and then standardizing it with 0.53 gram of  $\text{NaHCO}_3$ . If the acid is of proper strength, ten cc. of it will be needed to neutralize the sodium carbonate.

If a less amount is required, an additional quantity of water is added to bring it to the required strength; this can be calculated by simple proportion. The sodium hydroxide solution is made by dissolving forty grams of the pure NaOH in a liter of water. Its exact strength should be determined, and it is always best to make the solutions so that one cc. of the acid will equal one cc. of the alkali. The indicators used are phenolphthalein and methyl orange.

To determine the alkalinity of the solution take an assay ton by weight, or measure out twenty-nine cc., which

will be very close to that amount; if the solution contains cyanide, silver nitrate, in solution, is then added until a slight turbidity is produced. Phenolphthalein is then added, and standard sulphuric acid is run in to the end-point. Each cc. of the acid consumed is equivalent to 40 oz. troy, or 43.9 oz. av. of NaOH to the ton, as the equivalent alkalinity of the solution. Eighty parts of NaOH are equal to 56 parts of CaO.

**319. Acidity of Ore.** Ores are usually acid and seldom alkaline. Take one assay ton of the ore, finely ground, and shake it for half an hour in a flask; filter, and wash with water until all soluble matter is removed from the residue. Test with litmus paper to see if acid or alkaline, and run in enough sulphuric acid, or sodium hydroxide, to end reaction. Each cc. of NaOH used corresponds to 49 oz. troy, or 53.8 oz. av., of  $\text{H}_2\text{SO}_4$  per ton of ore. If the solution is alkaline, the standard sulphuric acid must be run in to neutral reaction, when each cc. used will correspond to an alkalinity of forty ounces troy per ton, expressed as NaOH.

**320. Determination of Cyanide in Solutions.** To ten cc. of the solution, or more, if weak, in a small flask, add one gram of precipitated lead carbonate and shake thoroughly to remove any sulphides; these are then filtered off and washed, when the solution is ready for titration. Five cc. of a solution of potassium iodide is then added as an indicator. This indicator solution is made by dissolving one gram of potassium iodide in a liter of water. A standard solution of silver nitrate is then run in to the first faint permanent yellow color. Making the silver nitrate solution by dissolving 6.519 grams of  $\text{AgNO}_3$  in a liter of water, and using ten cc. of the solution, each cc. of silver nitrate solution will represent one pound of KCN per ton.

**321. Determination of Silver and Gold.** Take an assay ton, or more, of the solution, place it in a beaker of sufficient size, place a V-shaped piece of sheet aluminum in the solution and add sulphuric acid to acid reaction, then boil. After a few minutes of hard boiling all of the gold will be precipitated in metallic form, together with the silver. At first some of the silver may be precipitated in the form of cyanide, but this changes to metallic silver by prolonged boiling. Remove the aluminum, washing off all the precipitated metals with a strong jet of water, filter off the metallic residue, dry quickly, and throw the filter into a scorifier with sixty grams of granulated lead, scorify and cupel in the usual way. The precipitation of gold and silver by aluminum is complete, as I have determined by many experiments, and I think its use will be found a great improvement on the methods now employed.

Aluminum is suggested as a precipitant on a commercial scale for gold and silver from cyanide solutions as a substitute for zinc by Carl Moldenhauer, who patented his process in 1893. The process failed for the reason that free acid was necessary in the solutions for the complete precipitation of the gold and silver, and as this is not practicable in the commercial extraction of values, it was bound to fail. As a laboratory method it will be found a success.

## CHAPTER XXXV

### ANALYSIS OF COMMERCIAL CYANIDE

Dissolve twenty grams of the substance in 150 cc. of water and filter off from any insoluble residue through an ashless filter, catching the filtrate in a graduated flask. Wash carefully. The filter is ignited and weighed, and the percentage of insoluble matter, which is  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ , calculated.

**322. Determination of Carbonic Acid.** Calcium nitrate is added to the flask, and after shaking, the flask is filled up to the mark, 250 cc., with water, shaken again, and allowed to stand for one hour. It is then filtered, the residue on the filter being  $\text{CaCO}_3$  proportional to the carbonic acid in the cyanide; it is washed, ignited, and weighed as  $\text{CaO}$ . The weight of  $\text{CaO}$  multiplied by 0.786 gives the weight of  $\text{CO}_2$  in the 20 grams of cyanide taken.

**323. Determination of Hydroxide.** The filtrate from the  $\text{CaCO}_3$  is diluted to 500 cc., of which 100 cc. are taken for the hydroxide determination. To this add a solution of magnesium nitrate and allow to settle for an hour, then filter off the precipitate of magnesium hydroxide, ignite in an annealing cup, and weigh as  $\text{MgO}$ ; this weight, multiplied by 0.85, gives the weight of hydroxide in four grams of the cyanide, from which calculate the percentage.

**324. Determination of Cyanogen.** Take 50 cc. of the 500 cc. and add five cc. of strong ammonia and five cc. of the potassium iodide indicator (see section 320). Then

run in the standard solution of silver nitrate. The CN factor is obtained from the Cl factor by multiplying it by 0.7324, and it will be about one cc. = 0.0036CN.

**325. Determination of Cyanate.** Take 50 cc. of the solution and add an excess of a strong solution of silver nitrate, which will precipitate all of the cyanogen and chloride combined with the silver, shake well, filter, and wash with ice cold water. After washing, place a clean flask beneath the funnel and pour over the filter ten cc. of a standard nitric acid solution, made by mixing 100 cc. of strong nitric acid with about 900 cc. of distilled water. The cyanate will act upon the nitric acid. The excess of nitric acid is determined by titration with a standard solution of sodium hydroxide. Each molecule of  $\text{HNO}_3$  corresponds to one molecule of CNO. Having determined the number of cc. of the normal nitric acid that have been consumed by the silver cyanate, as well as the weight of  $\text{HNO}_3$  in one cc. of the standard solution, the weight of CNO is found by multiplying the cc. of  $\text{HNO}_3$  by 0.6666, from which weight the percentage of CNO may be determined.

**326. Determination of the Chlorine.** Weigh out one gram of the powdered salt into a small porcelain crucible and heat it gradually, adding a mixture of five parts of  $\text{Na}_2\text{CO}_3$  and one part of  $\text{KNO}_3$  until all of the cyanogen is decomposed. Cool and dissolve the mass in water, acidify with nitric acid, and filter to clear the solution. The chlorine can then be determined by titration with a standard solution of silver nitrate, as in section 258, or it may be precipitated with silver nitrate and determined in the gravimetric way.

**327. Determination of Potassium and Sodium.** Decompose in a platinum dish 0.25 gram of the powdered salt, with dilute hydrochloric acid, being careful to perform the

operation under a hood with strong draft to avoid injury from the poisonous fumes; evaporate to dryness, and ignite to drive off all salts of ammonia; cool, and weigh as NaCl plus KCl. Then determine the potassium with platinic chloride and the sodium by difference as in 209.

**328. Remarks.** Pure potassium cyanide contains 40 per cent of cyanogen, and in the trade corresponds to 100 per cent cyanide. Ninety-eight per cent cyanide contains only 39.2 per cent cyanogen, and 125 per cent cyanide contains 50 per cyanogen. It has been found that potassium cyanide carrying sodium cyanide is more efficient than the pure article, owing to the larger percentage of cyanogen. There is economy in the reduction in freights, and also for the additional reason that the combined cyanide can be made and sold more cheaply than the pure potassium cyanide.



## CHAPTER XXXVI

### COMBINING DETERMINATIONS

One of the chief time consumers in analytical work is the time necessary for accurately weighing up the pulps for the various determinations. In many instances it is possible to make several determinations from the one sample weighed up, without loss of time in the necessary separations, thereby saving the time lost in weighing up a separate amount for each determination. Advantage is taken of all of these opportunities, and the judgment of the assayer will tell how far in this direction it is well to go. The following combinations can be safely followed without danger of reducing the accuracy of the methods:

**329. Insoluble, Iron and Sulphur.** Treat for insoluble in the usual way (270), using nitric acid for decomposition of sulphides and being careful to wash the insoluble with a boiling solution of ammonium chloride to ensure that all sulphur goes into the filtrate. Precipitate the iron with ammonia water, filter it off and wash well with hot water. Precipitate the sulphuric acid in the filtrate with barium chloride, as in section 286. Dissolve the iron hydroxide in the least amount of warm hydrochloric acid necessary for complete solution, add water, and reduce and titrate as desired in Chapter XI. The results are accurate except when barium sulphate is present in the pulps.

**330. Insoluble, Iron, Calcium, and Magnesium.** The insoluble and iron are determined as in section 329, and in the filtrate from the iron the calcium is determined, as

in section 74, and the magnesium in the filtrate from the calcium oxalate, as described in section 168. Results accurate.

**331. Copper and Iron.** Follow the method for copper down to the precipitation on aluminum. Save the liquor decanted from off the copper together with the washings. The iron is completely reduced and is ready for titration with the permanganate solution so soon as it cools to room temperature. It is well to add five cc. of dilute sulphuric acid previous to titration, to ensure that there is sufficient free acid to make a good titration. The copper is taken up with nitric acid, as in section 91, and determined by any standard method.

**332. Lead and Iron.** After filtering off the lead sulphate, the iron is reduced in the filtrate and determined as in section 140. The lead sulphate is dissolved as usual and the lead determined, as in section 155. The iron is liable to be a trifle low, as the lead tends to hold on to some of the iron sulphate.

**333. Lead, Copper, and Iron.** After decomposition and formation of the lead sulphate and filtering off, the filtrate is reduced with aluminum, precipitating the copper; then proceed, as in section 331. Results are accurate for the lead and copper and may be a little low for the iron.

**334. Zinc, Iron, and Insoluble.** Treat as usual for zinc (237). The iron and insoluble will be in the casserole or on the filter after the washing of the zinc out of the residue. Place a clean flask under the funnel, and after cleaning out the casserole by warming a little hydrochloric acid in it, pour it and fresh hydrochloric acid over the residue on the filter and wash it thoroughly. The insoluble residue remains on the filter and is dried, ignited, and weighed, while the filtrate contains the iron which is reduced and titrated by any convenient method.

## CHAPTER XXXVII

### ORE TESTING

The assayer is frequently required to make some preliminary tests on ores to determine the probable best method for beneficiating them. His tests can only be regarded as preliminary steps, and his recommendations should be tested on a large scale, at some of the many excellent testing plants, before any plan is definitely adopted.

In making his recommendations, a sample representing the mine run, of from fifty to one hundred pounds in weight, should be submitted. Examination and identification of the minerals, followed by a complete analysis, will usually suggest the general line of treatment. The following methods may then be tried:

**335. Crushing Tests.** Pass the ore through a laboratory crusher set to ten-mesh size. Then screen the crushed product through a series of sieves of 20, 30, 40, 60, 80, and 100-mesh. Weigh each size, and keep each separate, and calculate in percentage from the amounts of the different sizes, which will express in a general way how the ore will behave when crushed, always a question of serious importance.

Each size should be kept separate and samples cut out for assay.

**336. Concentrating Tests.** A weighed portion of each size is then concentrated in a pan, or horn spoon, and run down as far as deemed advisable, when the con-

centrate is dried and weighed. This weight divided into the weight taken gives the degree of concentration. The tailings from the operation may be caught, dried, and weighed. The weight of the tailings plus the weight of the concentrates will be usually less than the weight of the sample taken, and the difference may be regarded as slimes.

By assay of the original pulp and the concentrates, tailings, and slimes, the degree of saving is determined and the work checked. The following calculation explains the method.

We take one hundred grams of ore assaying 12 oz. silver and 6 per cent lead, and pan it, securing:

Grams.	Assay Value.			
8 Concentrates .....	105	oz. silver	and 58%	lead
90 Tailings.....	2.2	" "	" "	1.1% "
2 Slimes .....	55	" "	" "	12.5% "

	Units of Silver.	Units of Lead.
Pulp.....	1200 (100×12)	600 (100×6)
Concentrates.....	840 ( 8×105)	464 ( 8×58)
Tailings.....	198 ( 90×2.2)	99 ( 90×1.1)
Slimes.....	110 ( 2×55)	25 ( 2×12.5)
Units accounted for . . . . .	1148	588

Per cent of silver saved.....	$840 \times 100 \div 1200 = 70.0\%$
Per cent of lead saved.....	$464 \times 100 \div 600 = 77.3\%$

By panning the different sizes it is possible to learn whether one particular size will give a greater saving than another.

**337. Chlorination Test.** One hundred grams of the ore crushed to pass 40-mesh are placed in a 500-cc. flask. Moisten the ore with fifty cc. of water containing five cc. of sulphuric acid. Cover with 250 cc. of a saturated solution of chlorine in water, and shake it up every hour

for two days. Transfer contents of flask to a filter and wash four times with tap water, allowing all of the water from each washing to pass through before adding more. Dry, cut out a sample, and assay. The ore having been first assayed, the data are available for calculating the percentage of saving.

This test should be made on the raw and roasted ore. One hundred and fifty grams of the ore should be roasted in the muffle until no more fumes are given off. The roasted ore is then mixed and a sample cut out for the assay. One hundred grams of the roasted product are treated in the same manner as the raw ore.

By analysis of the raw ore and roasted product, the changes accomplished by roasting are determined.

**338. Bromine Test.** This is made like a chlorination test, section 337, on raw and roasted ores, using a saturated bromine water in place of the chlorine water.

**339. Amalgamation Test.** An ore will give up to mercury the same amounts of silver and gold that it will give up to a solution of sodium thiosulphate, or so nearly so that the saving with "hypo" may be taken for the saving with mercury.

One hundred grams of the ore crushed to pass forty-mesh are taken and shaken for three days in a liter flask with five hundred cc. of water, fifty grams of sodium thiosulphate and five grams of cupric sulphate; after it is thoroughly washed with tap water and dried the leached ore can be assayed. The percentage of saving is then easily calculated.

It is also advisable to roast one hundred grams of the crushed ore with ten grams of common salt thoroughly mixed in a roasting dish in the muffle, and lixiviate the roasted product as above with the "hypo" to determine the saving with a salt roast.

**340. Cyanide Test.** The first cyanide test should be made on ore crushed as fine as is possible to make it, 250 mesh if convenient. One hundred grams of it are then taken, first cutting out a sample for assay, and placed in a 2½-liter bottle and a liter of water holding in solution forty grams of commercial potassium cyanide added and shaken up. A current of air driven by means of a Richards filter pump should be passed through the mixture constantly during a period of six days, and the bottle thoroughly shaken once every six hours.

At the expiration of six days the liquor is decanted, or filtered off, and the residue thoroughly washed with tap water and then dried and assayed. If the raw or roasted ore does not show a leaching of at least seventy-five per cent by this method, it may be safely reported as not amenable to cyaniding.

If it shows a satisfactory saving, further tests may be made to determine the economic degree of fineness, the consumption of cyanide, and the other factors necessary to know to determine the advisability of cyanide treatment.

**341. Remarks.** The above rough tests may be carried as far as the interested parties wish, but no matter what recommendation may be made by the assayer, it would be unwise to order machinery until the tests could be repeated on a large scale, of at least of several tons, along the plan shown by the preliminary test as advisable.

## CHAPTER XXXVIII

### GENERAL SUGGESTIONS FOR YOUNG ASSAYERS

The young graduate coming out from school and thrown on his own resources in a mine, or smelter, laboratory, will frequently be at a loss to handle the volume of work thrown upon him, and it is my desire, in this chapter, to give him an idea of how to proceed. His work must be cleared up every day, and while it is hardly probable that he will not make some mistakes, he must stand, or fall, upon his daily results.

**342. Preparation of Samples.** As a rule the samples will be given to him ready ground for work; if not, a man will be given him to perform this labor who is also expected to look after the fires in the furnaces; unless the volume of work is small, in which event the assayer will have to prepare his own samples. This is an easy matter if there is a power plant for grinding, becoming more laborious with its absence.

The samples are first broken up to small size, if possible; so that all will pass a 10-mesh sieve; then it is thoroughly mixed and quartered down till the sample has reached a convenient size for fine grinding. If this has to be done on a bucking board, the sample finally pulped must be made small, to save time. But the assayer should keep his sample as large as possible, as he thereby diminishes the factor of error, which is always considerable in all sampling. As far as possible the samples should be prepared the evening before.

Small pans are most convenient for holding the samples, and after entering them in his record book the assayer should quickly learn to work without marking the samples at any period of his operations, but work entirely from position. If each sample is to be run for the same determinations the strain upon his memory amounts to nothing; if determinations vary for different samples a few penciled notes may be necessary at first, but if he records in his record book the determinations to be made for each sample no other note of any kind will be necessary.

It is a waste of time to mark vessels, crucibles, cupels, etc., and it is a cause of errors. In a few days' experience the young assayer will find that he can keep track of his work with unerring certainty. The order I work with is from left to right. Any other order may be adopted, provided it is adhered to by everybody handling the work.

In preparing the pulps they should be made as fine as possible. On the bucking board it is too laborious to make them finer than 120-mesh, but if machinery is available they should be made 200-mesh fine.

The finer the pulp the more nearly uniform in size are the particles, consequently more perfect and uniform mixture is possible; the surface exposed to the action of solvents and fluxes is increased and they act with greater efficiency and rapidity. There are now available grinding machines capable of producing quickly pulps of from 200 to 250-mesh in fineness. They should be more generally used. I have found regrounding very beneficial in securing accordant results, when previously no two results would check.

**343. Method of Working.** On arriving at the office in the morning the assayer should first see to the starting of his fires. Next, he should do his weighing up. If he has much wet work it is sometimes best to first weigh up



for the wet determinations and start their decomposition with acids, and while the acids are working weigh up for his fire assays.

The weighing up being completed, the fires are again looked at and, as soon as the furnaces are ready, the fire work can be started on its course. During the intervals, while they are heating, the wet work can be pushed along.

After the pulps are decomposed he can put the vessels on the hot plate and push their evaporation as rapidly as convenient.

As he withdraws the batch of crucibles, or scorifiers, from the muffle, he introduces a new batch, and when the slags are cooled enough he cleans the lead buttons and places them in order on iron trays, made and sold for that purpose. If it is necessary to rescorify any of the lead buttons before cupellation he should perform this in a No. 2 scorifier, placing a piece of slag on the tray in the place of the button which is being scorified. As he cupels, he does so in regular order, but it is unnecessary to mark their places on the tray while cupelling, if he marks the place of those he has to rescorify. If he has crucible work with regular scorification work, he will find it best to first run the crucibles before starting the scorifiers, and keep separate trays for his crucible and scorifying work.

The wet work is kept moving in the intervals when not filling the muffles. It is only in this way that a large volume of work can be kept going at a rate that will enable the assayer to finish his work the same day. He will have to be on his feet all of the time till the day's work is over. He will quickly learn to keep everything moving, so that by the time his cupellations are through, his insolubles will be ready to go into the muffle for ignition and his wet determinations will be standing in

their flasks, or beakers, ready for titration. At the first opportunity he weighs up all his silver beads and then puts them in their parting cups and parts them. While they are drying and cooling, after ignition, he finishes his wet work and winds up the day by weighing his gold and recording all of his results in the record book.

**344. Daily Volume of Work.** How much work can an assayer do in a day? This largely depends upon the facilities for handling work, as well as on individual ability. I have known an assayer in a day of ten hours, with a double muffle furnace, to make fifty separate assays for gold and silver, twenty-five fire leads, thirty insolubles and the same number of irons and limes; twenty-five wet leads; twenty coppers; ten sulphurs and eight manganese—in all 278 individual determinations. In doing this volume of work he had the assistance of a boy in looking after the furnaces and cleaning the lead buttons and he also had a large hot plate and excellent facilities for rapid handling of wet work. The greatest strain was to weigh up the charges and for several days thereafter the assayer was too fatigued to do accurate work.

Sixty determinations, daily, may be considered an average fair day's work about a plant where results must be accurate.

**345. Specimen, Control and Umpire Assays.** These will be some of the first terms the young assayer will hear. Specimen assays are the ordinary determinations where absolute accuracy is not expected. Control, comparison, or check assays are those results which must be compared with the results of others, consequently the assayer must be as accurate and sure of his results as it is possible for him to be. Such assays are usually made in duplicate, or triplicate, to diminish the possibility of error.

When two assayers do not agree near enough in their results on the same pulps, it is customary to send a sealed pulp to some assayer of well-earned reputation for careful work, who is supposed to give ample time to each determination, and his results are usually final in making settlements. It is, however, customary if his results fall below, or run above, the results of the control assays to ignore his findings and the result of the smelter or ore shipper's assayers are taken. This practice is the development arising from the mistakes made at times by umpire assayers. A great many persons think that the results of an umpire assayer are more accurate than the results of the assayers representing the ore shippers and ore buyers. This is a mistake, in many instances, for it must be borne in mind that the assayers working every day on the same ores learn the little differences and variations in treatment necessary to secure the most accurate results. While greater reliance should always be placed upon the results of an umpire assayer, it does not necessarily follow that his work is more accurate. The ore shipper, or ore buyer losing the umpire assay pays for it.

## CHAPTER XXXIX

### OBSERVATIONS ON TECHNICAL METHODS

**346. Balances.** For weighing out pulps for fire assays, where half an assay ton is used, the sensibility of the balance need not be greater than one milligram; in weighing up charges for scorifiers the sensibility should be one-tenth of a milligram; in weighing up half gram charges for wet determination the balance should have a sensibility of one-fiftieth of a milligram; the same sensibility as required for weighing silver buttons. For weighing gold buttons the sensibility of the balance should be at least  $1/500$  part of a milligram. The best balance usually furnished for analytical work is only sensitive to  $1/10$  milligram, making the error in weighing up half-gram charges, plus or minus 0.02 per cent. In rapid weighing this error is probably doubled. There is need for a short-beam analytical balance, provided with larger pans than the button balances have, for use in wet work. Its parts should be made light, but secure, and the maximum load should not be above five grams. Weighing must be done quickly and that can only be done with a short-beam balance.

The assayer should adjust his balances every day before beginning work and after concluding it, and test them as much oftener during the day as he can find time. Not so much because the balances need frequent readjustment, as for the reason that, unless the tests are made before and after each weighing, one cannot be certain that the

particular weighing was correct. It is not probable that the assayer can test before and after each weighing, but if it is possible to do so it should be done.

The weights of precision as sent out by first-class makers are not always accurately adjusted.

The eastern and foreign manufacturers of balances have no conception of the accuracy required by western chemists and metallurgists. It is not so long ago that one of our important government bureau officials offered to furnish weights guaranteed to have no greater error than plus or minus 0.02 of a milligram. The weights used for weighing silver and gold buttons should not have an error of more than plus or minus 0.002 of a milligram, and western manufacturers guarantee them plus or minus 0.005. The larger weights used need not be so accurate; but it is highly necessary that they be carefully adjusted and their accuracy tested at least once every month. I keep one set of weights in my office that are only used to test and adjust the weights employed daily. This set of standard weights is never handled by anyone except myself, and even with all my care I would not be willing to take oath that my weights are absolutely correct. I feel confident that they are above the average in accuracy.

One cannot rely upon the guarantees made by the manufacturers. I remember once buying a set of weights in which the manufacturer guaranteed the maximum error would be only plus or minus 0.01 milligram. There were three milligram riders in the set. One weighed 0.95 of a milligram, another 1.12 milligram, and the third 1.3 milligram. The gram weight was accurate, the two-gram weights were 2.12 and 2.14 respectively, the five-gram weight was 4.96 and the ten-gram weight 10.25. This set of weights was sent out by a reputable manufacturer under a positive guarantee. When his attention was called to the matter

he wrote that it was not possible to make weights of precision as accurate as he had guaranteed to make them.

**347. Varying Results.** The difference in results by different chemists, working on the same pulps, and using the same method, has been frequently noted and commented upon, usually to the disparagement of the method. It is my opinion that many, if not all, of these criticisms should be directed against the analyst and not the methods. There is considerable difference between following a method and actually carrying out the method. Different chemists slur different details of the methods. They do not seem to appreciate that each step in the method is intended to accomplish a certain definite purpose at that particular moment and unless that purpose is accomplished an erroneous result is sure to follow. The fact that a method can be safely modified to suit particular cases has been known to result in a conclusion that, thus modified, the method may suit all possible cases. The errors that have come from such conclusions are too painful to enumerate.

The young chemist must never fail to remember that every detailed step given in the descriptions of technical methods of analysis has been put there because in some classes of ores it has been found necessary that it should be included. In general laboratories, receiving work from all sections of a mining country, the analyst must have a method that will suit any possible conditions that may be sent in, consequently he follows methods which may be, in some cases at least, longer than necessary. In those instances where work is done on one variety of ore at all times, it is usually possible to shorten up the method very much. This is proper; but do not rush to the conclusion that because your modification, for the possible variations you have, in your limited experience, is found

to be all right, it is safe to apply it to everything that comes along.

Differences in results by different chemists working on the same pulp are also due to imperfect pulverization and mixing of the pulps; using coarse balances for fine work and fine balances for coarse work; imperfect decompositions and imperfect separations; and failure to use correctly adjusted weights.

**348. Decomposition.** In my opinion the greatest errors made by chemists are at the time of the acid treatment of the pulps.

It is customary to put in the proper amount of acid and almost immediately put the vessels on the hot plate, when the acid begins to boil off more rapidly than the water, and, very quickly, instead of having strong acid decomposing the pulp there is nothing but acidulated water trying to accomplish the impossible. In no instance should the assays be put on the hot plate until after they have acted for half an hour at a temperature not to exceed 40° C. A shelf in the window facing the south, if there is plenty of sunshine, is an ideal place for the first twenty minutes of the decomposition period. A little experience will teach the analyst to recognize the degree of decomposition. This is a very important matter, equally as important as accurate weighing.

**349. Evaporation to Dryness.** This is usually the second step in every wet method. This must be done quickly, but not so rapidly as to cause loss by spattering. A water bath is too slow for use in a technical laboratory, and it is never employed except when absolutely necessary. Hot plates, so heated as to have different temperatures at different points are the best thing. If electricity is cheap there is nothing better than an electric hot plate. Steam-heated plates are the next best.

Beyond these it is just a question of using the best thing one can get.

**350. Variations in Methods.** The assayer should understand the reason for every operation, and he should see that the purpose of every treatment should be accomplished. Simply following instructions is not enough. There should be no variation in the method, unless experience shows it to be necessary or desirable. In volumetric work, in particular, close adherence should be kept to the directions about bulk. Too much stress is laid by technical analysts upon the value of "check," or "duplicate," assays. One assay *carefully made*, where the assayer can say "I know that each step in the method was rigidly followed and its purpose accomplished," is of far more value than any number of checks in no one of which the operator can make a like statement. When duplicate assays are run at the same time, they are pretty sure to receive precisely the same treatment, consequently any error in the treatment of one is pretty sure to occur in the other, so they are almost sure to check, even when the work is done by a poor analyst. Duplicates made at different times on succeeding days are of some value if they check reasonably well.

**351. Errors in Burette Reading.** Burettes are graduated to one-tenth of a cc., but it is possible to guess to one-twentieth of a cc., which is the limit, as two or three drops of a solution is equal to one-tenth of a cc. In volumetric work half a gram of ore is taken and the strength of the standard solutions is so made that each cc. will correspond to one per cent; consequently the errors from burette readings cannot be less than plus or minus 0.05 per cent, and is probably always plus or minus 0.1 per cent. If greater accuracy is required, possibly it may be obtained by first using a strong



standard and finishing the titration to end-point with a standard one-tenth the strength of the normal standard.

**352. Errors in Results.** There is no operation in which there is not a factor of error. Besides the instrumental, mechanical, and chemical errors, there is the individual factor, peculiar to each analyst, and which must be more or less unknown. The errors are plus and minus and the plus errors of one stage *may* balance the minus errors of another, but this is mere speculation. In fire assaying for silver the error is probably minus at all times, running from minus 0.5 per cent to possibly minus 2.0 per cent. In assaying for gold the error is also probably minus, varying between 0.01 per cent to minus 0.2 per cent. In wet work the errors are plus and minus. The error from imperfect separation is too variable to permit an expression of any value. In weighing, the error is plus or minus 0.02 to 0.4 according to the kind of scales used. In burette reading the error is from plus or minus 0.05 to 0.1 per cent, consequently wet results by different assayers on the same pulps, which do not vary more than 0.2 per cent may be regarded as good checks.

When the differences in results by different assayers exceed these limits, poor work has been done by one or all the analysts.

## CHAPTER XL

### ORE CONTRACTS AND MEXICAN TAXATION ON ORE PRODUCTION

In buying silver-gold ores the smelters classify the ores into lead ores, copper ores and siliceous ores and the shipper is likely to be asked to contract the sale of his ores in a duly signed contract containing approximately the following clauses:

"A.B." agrees to sell to the "Phoenix Smelting Co.," for a period of one year all of the ores (copper, lead, or siliceous) produced by the "Lone Star" mines, at the rate of five hundred tons monthly.

In the event that the mine produces more than five hundred tons monthly, the Phoenix Smelting Co., shall have the right to purchase the excess on the same terms and in the event that the company does not care to buy the excess A. B. shall have the right to dispose of it as he sees fit.

Should the entire amount of six thousand tons not be delivered within the year, A. B. obligates himself to deliver the amount lacking after the end of the time named under the terms of this contract provided the mine produces the ore.

The ores herein contracted for shall be delivered at the smelter of the buyer and it is agreed that any change in the now existing railway freight rates on this ore shall be for the account of the shipper.

The buyer shall have the right to divert these ores to

any other point designated by him, but any change in freight rates due to said change shall be for the account of the buyer, and the seller shall have the right to have the ores sampled at the first named place of delivery.

The sampling of the ores shall be conducted in accordance with the usual commercial methods, cutting out one-tenth part of the shipment to make the final sample, after quartering down. The shipper shall have the right to witness the sampling in person, or by properly accredited representative, and shall have the right, during the progress of the operation, to make objections to the manner of conducting the same, if he thinks the sampling is not made in a proper manner.

The final sample, pulped in the bucking room, shall be thoroughly mixed and divided into six envelopes, two of which properly sealed shall be delivered to the shipper, or his representative, and two shall be mutually sealed to be delivered to an umpire assayer, should it be impossible for the buyer and seller to agree upon the assays and analysis of the sample.

In the event that an umpire should be necessary, the samples to be umpired shall be sent in rotation to "A," "B," and "C," and their results shall be final, provided that if they differ from the results of the assayers of the buyer and seller, that result shall be selected which is between the highest and lowest results of the three sets of results. The cost of the umpire shall be for the account of the party losing the same.

The moisture in the ore shall be determined in the conventional manner by the buyer, and it shall be deducted from the brute weight of ore in the cars received. Should the determined moisture be less than one per cent, nevertheless one per cent moisture shall be deducted.

The loaded cars shall be weighed in the presence of the representative of the shipper on the car scales in the smelting yard, and when emptied the tare shall be determined in like manner.

The method of making the various determinations shall be by the usual commercial methods. Silver by the scorification assay; gold by the crucible assay; lead by the fire method [*Note.*—If by the wet method, then two per cent shall be deducted from the wet result], copper by the wet method, electrolytic or volumetric. It is understood that where "dry copper" in this contract is mentioned it is the wet result less 1.3 per cent.

Lots of powdered ores and concentrates of which 25 per cent will pass a  $\frac{1}{4}$ -inch mesh screen shall be subject to a briquetting charge of \$1.50 per ton.

Shipments in lots of less than five tons shall be subject to a sampling charge of three dollars per lot.

All silver in the ore shall be paid for provided there is one ounce or over, at the rate of 95 per cent of the New York quotation on the date of sampling, which shall be the date of receipt of the last car of the lot.

All gold in the ore shall be paid for, provided there is not less than one-tenth of an ounce troy in the ore, at the rate of \$19.00 per ounce. If more than one ounce it shall be paid for at the rate of \$19.50 per ounce.

All lead shall be paid for provided there is five per cent of lead, fire assay, at the rate of twenty-five cents a unit when the price of lead in New York is \$4.00 per hundred pounds, and for every variation of five cents per hundred in the price of lead in New York there shall be an addition, or reduction as the case may be, of one cent per unit.

[*Note.*—If this ore originates in Mexico the lead is paid for at the rate of one cent (U. S. currency) per pound

when lead in London is £13 per ton 2,240 pounds, only paying for 90 per cent of the fire assay lead content. For each variation in the London price of 1s. 6d. add or deduct  $1\frac{1}{4}$  cents (U. S. currency) per hundred pounds.]

All copper shall be paid for provided there is three per cent of copper, wet assay, in the ores, at the rate of ninety per cent of the wet assay content at New York selling price for electrolytic cathode copper less two and one-half cents per pound. No payment will be made if less than three per cent is contained.

All iron will be paid for at the rate of five cents for each unit contained.

All manganese will be paid for at the rate of five cents for each unit contained.

All lime will be paid for if not less than three per cent at the rate of five cents for each unit contained. Lime combined with fluorine will not be paid for.

A charge of ten cents per unit shall be made for all insoluble matter in the ores.

A charge of twenty-five cents will be made for each unit of sulphur contained, but in no case shall the maximum charge for sulphur exceed \$4.50 per ton.

A charge of twenty-five cents will be made for each unit of arsenic, antimony, and bismuth in the ores, separately or combined, provided there be at least three per cent of the combined metals.

A charge of twenty-five cents will be made for each unit of zinc in excess of eight per cent.

A charge of five dollars per ton of 2,000 pounds will be made on all ores carrying five per cent of lead, or less. If over five per cent of lead deduct from the smelting charge fifteen cents for each unit in excess of five per cent.

[If the ores are copper ores, the following will be sub-

stituted for the preceding clause: A charge of six dollars per ton will be made for all ores carrying three per cent of copper or less, and for each unit in excess of three per cent deduct twelve and a half cents from the smelting charge.]

The quotations used in this contract shall be: For silver, that of the New York Metal Exchange for the day of sampling. For lead, the quotation of the *Engineering and Mining Journal* of New York in the last number preceding the day of sampling the lot. For copper, the quotation of the *Engineering and Mining Journal* of New York for electrolytic cathode copper made in the last number preceding the day of sampling of the lot.

In the event of acts of nature, strikes of any kind affecting the operations of the contracting parties or either of them; fires, floods, traffic interruptions; wars or insurrections; government regulations, or any other cause beyond the control of the contracting parties, or either of them, making it a disability or serious hardship to deliver the ores, or for the buyer to receive, purchase, and smelt these ores, the parties to this contract are relieved of all responsibility for damages, but shipments and receipts of the ores shall be resumed as soon as the disabling cause is removed, and this contract shall be prolonged for a period equalling the period of delay.

The usual paragraphs to make this contract legally binding are then added, and the validity of the signatures duly attested.

**353. Remarks.** In the preceding outline contract, clauses showing manner of payment for both lead and copper are included.

Copper ores carrying lead are not desirable ores for copper smelters, and likewise lead ores carrying copper are undesirable in the lead smelter.

The predominant base metal is usually the only metal paid for; but I have known instances where the smelter paid for both copper and lead, but the rate paid for each metal was considerably lower than the usual rates.

If the ores originate in Mexico, clauses are added covering the payment of taxes on the sales and production of the ores levied by the government. These taxes are always for the account of the seller, but there are different ways of caring for them, varying with the terms of any concessions held by the mining or smelting companies. The seller of the ores always bears the expense of these taxes, as is right and proper.

**354. Mexican Ore Taxation.** The ore producer in Mexico is required to pay upon his production a tax of four and fifty-five hundredths per cent to five and fifty-five hundredths per cent, distributed as follows:

A *bullion tax* of two and a half per cent on the gross value of the gold and silver in his ores. This is paid to the Federal government. If the ores are shipped outside the country, this tax is three and a half per cent.

A *production tax* paid on the gross value of his ores, as shown by the smelter settlement sheets. This is one and one-half per cent, and is paid to the State. To this is added twenty per cent to be paid to the Federal government, making a total of one and eight-tenths per cent.

A *factura tax* paid in stamps and levied by the Federal government based upon the net smelter returns, and amounting to one-fourth of one per cent.

All the above taxes are based upon the settlement sheets of the smelters, and no ore producer can escape paying them. If he is a small shipper, the revenue agent will require him to make a deposit of from five hundred to one thousand pesos, for which no receipt will be given,

and the railway agents will report to this agent every shipment made by the mine, whose manager will be called upon to furnish the corresponding settlement sheets and pay the taxes. The agent will evade giving a receipt for this deposit on various pretexts and is likely to have forgotten all about it when the mine ceases to work and the return of the deposit is asked for.

The above constitutes what may be termed the *direct tax*. In addition there are other items of taxation which must be borne by the mine which may be termed *indirect taxes*, these are:

A *factura tax* is levied on all supplies bought by the mine; it is paid by the merchant selling the goods, who always itemizes it in his bill. This varies in the different States, and the minimum is one and eight-tenths per cent.

When the mine has a store, it pays a tax on all its sales; there is the *factura tax*, the same as before mentioned; a tax on the total sales, which is generally partly evaded, and stamps which must be placed upon the books to legalize them, a proceeding that cannot be neglected, as there is always a possibility that the manager will some day have to produce these books in the courts, and if they are not stamped they are worthless as evidence. These taxes are of course placed by the mine upon the mine laborers, but as the income of the laborer depends entirely upon the mine and its production, or the ability of the stockholders to make up deficiencies, it seems to me that this may also be regarded as a tax expense that must be borne by every operated mining property in the Republic. This constitutes a high per cent when the expense account of the mine equals or exceeds the income from production; but in the largest and best properties in the Republic it is so small as to be unnoticeable.



The producers of lead ores have also to bear an additional *indirect tax* on the value of their lead product, at least seven per cent of the gross value of the lead in the ores.

On the system of payment for lead in ores in the United States the producer of a forty per cent lead ore receives \$13.20 per ton of 2000 pounds when lead is selling in New York at \$4.40 per 100 pounds. This is thirty-seven and a half per cent of the value of the 800 pounds of lead in the ores when sold on the New York market. The prices in Mexico are based upon the London market, which averages one and one-half cents per pound less than the New York prices. While the American producer receives for his lead fifty five-per cent of its London value, the Mexican forty per cent ore receives only \$7.28 per short ton, or thirty and one-half per cent of its London value. A large part of the difference of twenty-four and one-half per cent is undoubtedly due to the artificial conditions produced by the tariff laws in the United States, but seven per cent of the difference at the very least can only be regarded as an *indirect tax* borne by the lead miner in Mexico for the privilege of mining in that Republic. It is a just tax perhaps, for the smelters in Mexico pay greater taxes on their business than they would have to pay in the United States, or perhaps in other countries, and the producer is made to bear it just as he would have to do in any other country.

## CHAPTER XLI

### INFORMATION FOR SHIPPERS OF ORES CONCERNING PROCESSES OF SAMPLING AND MAKING SETTLEMENTS

**355. Contracts.** Before shipping any ore, the owner should have an understanding with the buyer as to payments and charges. The ore buyers will cheerfully send quotations to any probable shipper asking for information. The smelters prefer to make contracts, covering time periods, for all possible shipments, and always make better terms than they offer for "open" shipments.

Ore buyers have schedules applicable to all classes of ores, and can only vary from them within certain specified limits. If the shipper insists on better terms than those the agent can offer, the matter is referred to the district manager, who has power to make better terms for desirable ores that can be shipped in large quantities.

**356. Shipments.** The weight of the lot should be as large as convenient. The best results are secured, except in special cases, when the lots are not less than twenty tons; and if all the cars containing the lot can go forward promptly it is advisable to make the lots contain as much as 500 tons.

The bill of lading, together with a letter of advice containing all information possible to give, should be sent to the consignee, and a copy of this letter sent to the party who is to represent the shipper.

**357. Representation.** Every shipper has the right to be present in person, or by representative, at all of the

operations of sampling. The ore buyers desire his presence during the whole period, so there can be no question of unfairness or reasonable cause for dissatisfaction.

Usually the shipper employs one of the firms located near sampling works to attend to all of these matters for him; or he may send somebody from the mine; the more experienced the representative the more satisfactorily will all the operations proceed.

**358. Weighing.** The cars are weighed on track scales when they enter the smelter yards, in the presence of representatives of the smelter and shipper. After the cars are unloaded, their tare is determined and the "brute weight" found.

If the ore is sacked, the ore is weighed as it is unloaded, the sacks emptied and their tare determined to obtain the "brute weight."

If there are no track scales, the ore is hauled out of the car in wheelbarrows, and each barrow weighed as the ore goes to the sampling floor. The tare is calculated by weighing each of the wheelbarrows employed, and their average taken; this, multiplied by the number of weighings, gives the tare.

When weighing, each representative immediately compares his readings, and any difference is immediately corrected.

**359. Moisture Sample.** This is taken when the car is opened. If the ore is wet, it dries out as it is handled; if it is dry, there may be considerable loss in handling, and for this reason, as well as others, it is desirable to wet it down as soon as possible.

A representative of the smelter takes this sample. The representative of the shipper has the right to call the attention of the superintendent of the sampling plant to the matter when he thinks the sample is being taken

unfairly. The smelter people will always, if it is possible to do so without actual injury to their own interests, take this sample as the shipper wishes it to be taken.

If the ore is apparently dry, the moisture man goes over the surface, taking grab samples from various points in the lot. If it is moist, the top layer is removed at two different points, and a pit, or trench, made near the bottom of the pile, and the samples are taken from the sides of these openings. Duplicate samples are taken, amounting to about 50 ounces each. These samples are carried to the drying room, where they are first weighed, and then kept at a temperature of not above 105° C. until their weight is constant. The loss of weight is calculated as the percentage of moisture.

The moisture sampling is the only operation in sampling ores which may be adversely criticised. It is only an approximation of the true moisture content, since it is always based upon a "grab sample." I do not see any possibility of improvement in this operation, and it will be always possible for the shipper, or buyer, to be injured by an erroneous result. Naturally, the shipper always believes that he is the sole party injured, but I have invariably found the smelter people making an effort to be fair. If the shipper is not unreasonable in his demands the smelter people will satisfy him.

**360. Cutting Out the Sample.** This is the most important period of the entire process, controlling all following operations. All of the ore, unless already fine enough, is put through a crusher, large lumps being first broken up with sledges as may be necessary. The sample may be cut out automatically, by a machine, or by hand, according to the terms of the contract between the shipper and buyer. It is the custom to cut out one-tenth part for the sample, except in the case of high-grade ores, when

one-fifth part is cut out. This, the first cut, is crushed again, and one-fourth part cut out by automatic machine, or by hand. If the cut is made by hand, the sample is ringed and coned one or more times before the second cut is made.

The second cut is then crushed finer by running it through the rolls, and one-fourth part cut out, as before. This, the third cut, is ringed and coned from one to four times, as deemed advisable, and then cut down in 1:1 cuts, taking opposite quarters, alternately, until the sample weighs about 500 pounds. This, the "last cut," is equally divided into two parts; one is called the "original" and the other the "check" sample. Each is separately rolled and screened until all passes a 10-mesh screen. This is termed the "finishing roll," and metallics may be found on the screens; these are carefully collected, weighed, and divided into two equal parts, one for the shipper's, the other for the smelter's, assayer. If metallics are found, the samples rolled are weighed so that the metallics may be paid for. It will be readily seen that, when the sample rolled is about 250 pounds, it is necessary in the case of silver metallics, that they should weigh one-eighth of an ounce, in order to increase the value of the ore by as much as one ounce of silver to the ton. It frequently happens that the amount of metallics may be neglected.

The screened samples are then carried to the "plate" room, where they are carefully twice ringed and coned, after which they are cut down by 1:1 cuts to 30 to 50 lbs. The final plate cuts are sent to the drying room and dried. They are then ground in a "coffee" mill, so that all will pass a 30-mesh sieve.

The finely ground sample is then thoroughly mixed and cut down by "riffing" until there remains from 2 to

4 lbs. This is then "bucked" until all of it passes a 120-mesh sieve. On this sieve metallics may be found, which are collected, weighed, and assayed like the metallics from the finishing roll.

Finally, the completed pulp is carefully and intimately mixed and divided into six equal parts, which are placed in envelopes; two of these are given to the shipper, two are for the smelter, and two are mutually sealed and reserved for the use, if necessary, of the umpire assayer.

**361. Automatic Sampling.** The smelters prefer automatic to hand sampling. The relative merits of automatic and hand sampling is a matter of much discussion, with the argument in favor of automatic sampling, since most large shippers are in accord with the smelters. In the discussions I have read I have not noted that the real causes for difference of opinion have been properly emphasized. It is not so much the imperfections in automatic machines as it is in the condition of the ore before the first cut is made, taking into consideration the richness of the ore, and the size and frequency of the shipments.

The more uniform the ore, before cutting out is begun, the greater the certainty that any kind of sampling will be satisfactory; the larger the size of the lot the greater is the probability that errors in cutting out will balance each other; the more frequent the shipments from a property, the greater is the probability that errors in sampling one lot may be balanced in another. Under conditions it is easy to understand why the smelters and large shippers should be thoroughly satisfied with automatic sampling.

But the irregular shipper, particularly of small lots of high-grade ore, views the question from a standpoint entirely different; his chances for the equalization of

errors are very small as compared with the ore buyer's; his interests can only be well protected by the finest crushing and most thorough mixing possible, before any cut is made. It is not desirable to crush and roll an ore to a fine degree of subdivision for smelter use, to say nothing of the time and cost of such an operation, particularly on a large-sized lot. Neither is it possible to say how many times a lot should be ringed and coned before it will be so thoroughly mixed that all errors in the cuts will balance each other.

I believe that it does not make a particle of difference whether the sample is cut out automatically, or by hand; the entire question is simply one of condition of the ore before the first cut is made. Each ore presents its own particular problem as to preliminary treatment; what has been found satisfactory for one kind of ore may not give satisfactory results with another. In handling some high-grade concentrates of 30-mesh size, which had become somewhat lumpy from overheating when dried in a kiln, or from other causes, I found it absolutely essential that the entire lot be screened and all lumps broken up before ringing and coning; which was done four times before the first cut was made, although the lot was less than two tons in weight. These concentrates were no richer than a certain ore which was shipped in lots of about ten tons each, where satisfactory sampling was secured by crushing the entire lot to half-inch size, ringing and coning three times, cutting down by 1:1 cuts, and taking opposite quarters, alternately, until reduced to about 1,000 lbs. This cut was then recrushed, rolled, and screened through a 10-mesh screen, and coned and ringed three times, after which it was handled as any other sample.

In all instances when the sampling results were found unsatisfactory, I have always found the best remedy in

finer crushing and more intimate mixing before making the first cut.

It is easier to get satisfactory results in sampling high-grade material if the size of the lot is not more than ten tons. If the automatic machine can be thoroughly cleaned, before and after the operation, without the expenditure of a large amount of time and labor, I would prefer to sample with most any standard machine, provided always that the lot be well enough crushed and intimately mixed before any cut is made.

**362. Fairness of Sampling.** There is no operation in ore settlements more subject to suspicion by infrequent shippers than that of sampling; while I, like every other person with experience, consider it the most open, the fairest and least deserving of adverse criticism. In small agencies, acting independently, buying ores so as to make the largest possible profits by reselling the ores to the smelters, there is sufficient temptation for all of the trickery I have heard asserted, from time to time, by some shippers; but I know nothing of such matters, for all of my experience has been with companies who were in the business as a permanent thing, and desired to give even the least important shipper a square deal, relying solely on their regular schedules for the profits they desired to secure. With such companies I have always found but one ambition in the sampling department, viz., to do the work so well that resampling will be unnecessary. If a resample is called for, it is made cheerfully, and they are best pleased when the results of the resample check the first.

I have found that most of the adverse criticism of the sampling operation is based upon a lack of information on the part of shippers of the real facts, consequently, in this chapter, I have gone into a mass of detail which



may appear to be a waste of time. If I succeed in the slightest degree in removing any misapprehension in this matter I, at least, will feel the effort well repaid.

A great deal of the criticism is based upon imperfect sampling at the mine. It is natural for a shipper who finds the smelter results below the mine results, to jump to the conclusion that the mine sampling was right and the smelter wrong; investigation usually shows the mine sampling to be too much in the nature of a "grab" sample to make the mine results worthy of consideration. I find that when the mine sampling is done as carefully as it is done at the smelter, the results check closely. I also find the smelter samples to be from ten to fifty per cent higher than the mine samples almost as frequently as I find them below.

**363. Assaying Pulps.** The determinations made on pulps for ore settlements are termed "control," "check," or "comparison" assays. The smelter assayers are very careful in making their determinations for silver, gold, lead, and copper, and as they pay for these values, it seems to me they ignore their higher results, only reporting their lower, or the average of all. The assayer acting for the shipper apparently ignores his low results, probably to increase the chances of the shipper getting pay for the full content of the ore. The difference in the results of the two assayers not only represents the difference in results due to the errors in assaying, but also the difference in ability of the assayers themselves. When both assayers are equally skillful, the difference is generally so slight that a "split," the average of the two, is made. Otherwise an umpire inevitably follows, whose results are final, provided they are between the results of the smelter and shipper.

In the "insoluble," iron, lime, and like determinations, I

am informed that duplicates are seldom made by smelter assayers, consequently the shipper must see that he does not suffer from any possible errors in these determinations. The smelter probably relies on any errors in these determinations to balance each other in the long run, a chance which the shipper cannot afford to take.

**364. Differences Umpired.** When the assayers representing shipper and smelter are equally efficient, an equally efficient umpire assayer will report a result somewhere between the two. If he does this generally he acquires a deserved reputation for skill. It can be seen readily that a good umpire assayer should not only be a skillful assayer, but should also possess something of a judicial temperament to rightly interpret his results. The assayer representing the shipper must be as skillful and accurate as any umpire assayer, and should also be able to judge from his results the result that a good umpire will most certainly report; as he must work for the protection of the interests of the shipper, he is likely to be more than ordinarily particular, and may possibly go to umpire on abnormal differences, which will cause him to lose the umpire. A control assayer can lose very quickly a hard-earned reputation by losing a few umpires.

The amount of the differences which should be umpired vary with size of the lot and the value of the substance in which the difference exists. I consider it good policy to umpire any difference that amounts to \$8.00 on the lot; not on account of the amount of money involved, but for the reason that it stimulates the best work on the part of the assayers. A difference of one-tenth of one per cent in a copper determination on a 250-ton lot of ore would make a difference of \$50.00; such a difference should be umpired on account of the amount, although I consider it very good work for technical assayers to have no greater

difference than one-tenth of one per cent in a copper determination.

Different shippers have varying ideas concerning the amount of differences that should be umpired. The following represents about what should be umpired in a 50-ton lot:

Gold .....	0.01 ozs. troy per ton
Silver .....	0.40      "      "
Lead .....	0.5 per cent
Copper .....	0.1      "
Sulphur, zinc, etc. ....	0.5      "
Iron, lime, manganese .....	1.5      "
Insoluble .....	1.0      "

Some shippers wish all shipments umpired in those instances where less than one-tenth of an ounce of gold, of five per cent of lead, is not paid for, provided the control assayer secures one result only that does not fall below the limit; they argue that in such instances there is a reasonable probability that the umpire, if very careful, will get results that will compel him to report a result up to the limit, and if they only win one in ten, such umpiring will pay. In such matters there is ample room for difference of opinion.

In addition to the ordinary differences that are umpired, extraordinary differences occur at long intervals due to temporary inefficiency on the part of one of the assayers. These may be dismissed with the suggestion that the shipper who looks after his sampling and settlements will never suffer any losses from this cause.

A good control assayer is required to have a great deal of confidence in his ability; any assayer who is inclined to think that his results are inaccurate, when he learns

that another assayer reports different results on the same pulp, is of no value to anybody in the matter of assaying for ore settlements. Still it must be remembered that abnormal confidence cannot take the place of deficiency in skill.

**365. Settlements.** After the first assays have been made and the results show that the sampling was well done, the ore is released, which authorizes the smelter to put it in the ore bins, while the assayers are still working to find the actual settlement values.

If the differences are not too great, it is customary to split, but I believe it is always best to umpire most differences, for the habit of splitting is not, in my opinion, conducive to good work on the part of the assayers.

In some localities, instead of going to umpire, the custom of "joint assays" prevails. In this practice the assayer representing the shipper goes to the smelter assay office, or possibly to another assay office, to watch the smelter assayer make the assays. I do not consider this method free from criticism of a serious character from the shipper's standpoint.

If an umpire assay is determined upon, the shipper has a right to receive at least 85 per cent of the net value of his shipment, as shown by the results of the smelter. Since the custom of ignoring umpire results when they fall below the smelter, or go above the shipper, results, has become an established custom, there is no valid reason why the smelter should not immediately pay full value, making corrected settlements when the umpire results come in.

The old style of doing business, when the buyer did all he could to force the shipper to accept his results, sending the pulps for umpire to remote points, and prolonging, as far as possible, the time when payment will be made,

no longer exists, except, perhaps, with the small smelting plants. Everything is now conducted on a strictly business basis; besides handling the shipments expeditiously and fairly, efforts are made to show the shipper that he is given fair treatment; his complaints are listened to, thoroughly investigated, and faults, when found, are cheerfully rectified. The smelters with their great experience know the profits they must earn to obtain the large amounts of money needed to handle their business; their cost sheets have been tested and their schedules are made to yield the profit they must have. They are content with their legitimate profit, for the capital invested is so great they cannot afford to take risks for abnormal profits, that would invite active competition, likely to be disastrous should they have the ill will of the ore producers.

The shipper of high-grade ore still believes he should receive the low-treatment charges that the smelters give to low-grade ores; he is unwilling to recognize that the prosperity of the smelting industry, and the mining as well, requires large quantities of low-grade ores to carry on their gigantic business; that without them the treatment charges for high-grade ores would have to go back to the extremely higher rates of years ago. The low-grade shipper, likewise, is continually asking for better rates, as he works on a very narrow profit margin. Between the two conflicting mining interests, the smelter owners and employees pursue the even tenor of their way, patiently and courteously, doing the best they can for each interest involved.

# PART IV

## TABLES

### ATOMIC WEIGHTS

Name.	Sym- bol.	Atomic Weight.	Name.	Sym- bol.	Atomic Weight.
Aluminum.....	Al	27.1	Neodymium.....	Nd	143.6
Antimony.....	Sb	120.2	Neon.....	Ne	19.9
Argon.....	A	39.9	Nickel.....	Ni	58.7
Arsenic.....	As	75.0	Nitrogen.....	N	14.0
Barium.....	Ba	137.4	Osmium.....	Os	191.0
Bismuth.....	Bi	208.5	Oxygen.....	O	16.0
Boron.....	B	11.0	Palladium.....	Pd	106.5
Bromine.....	Br	79.96	Phosphorus.....	P	31.0
Cadmium.....	Cd	112.4	Platinum.....	Pt	194.8
Cæsium.....	Cs	132.9	Potassium.....	K	39.15
Calcium.....	Ca	40.1	Praseodymium....	Pr	140.5
Carbon.....	C	12.0	Radium.....	Ra	225.0
Cerium.....	Ce	140.25	Rhodium.....	Rh	103.0
Chlorine.....	Cl	35.45	Rubidium.....	Rb	85.5
Chromium.....	Cr	52.1	Ruthenium.....	Ru	101.7
Cobalt.....	Co	59.0	Samarium.....	Sa	150.3
Columbium.....	Cb	94.0	Scandium.....	Sc	44.1
Copper.....	Cu	63.6	Selenium.....	Se	79.2
Erbium.....	E	166.0	Silicon.....	Si	28.4
Fluorine.....	F	19.0	Silver.....	Ag	107.93
Gadolinium.....	Gd	156.0	Sodium.....	Na	23.05
Gallium.....	Ga	70.0	Strontium.....	Sr	87.6
Germanium.....	Ge	72.5	Sulphur.....	S	32.06
Glucinum.....	Gl	9.1	Tantalum.....	Ta	183.0
Gold.....	Au	197.2	Tellurium.....	Te	127.6
Helium.....	He	4.0	Terbium.....	Tb	160.0
Hydrogen.....	H	1.008	Thallium.....	Tl	204.1
Indium.....	In	115.0	Thorium.....	Th	232.5
Iodine.....	I	126.97	Thulium.....	Tm	171.0
Iridium.....	Ir	193.0	Tin.....	Sn	119.0
Iron.....	Fe	55.9	Titanium.....	Ti	48.1
Krypton.....	Kr	81.8	Tungsten.....	W	184.0
Lanthanum.....	La	138.9	Uranium.....	U	238.5
Lead.....	Pb	206.9	Vanadium.....	V	51.2
Lithium.....	Li	7.03	Xenon.....	X	128.0
Magnesium.....	Mg	24.36	Yttrium.....	Y	89.0
Manganese.....	Mn	55.0	Zinc.....	Zn	65.4
Mercury.....	Hg	200.0	Zirconium.....	Zr	90.6
Molybdenum.....	Mo	96.0			

## CHEMICAL FACTORS

	Weighed.	Required.	Factor.
Aluminum.....	Al	Al <sub>2</sub> O <sub>3</sub>	1.8888
	Al <sub>2</sub> O <sub>3</sub>	Al	0.5303
	AlPO <sub>4</sub>	Al	0.2214
	.....	Al <sub>2</sub> O <sub>3</sub>	0.4185
Ammonium.....	(NH <sub>4</sub> Cl) <sub>2</sub> PtCl <sub>6</sub>	NH <sub>3</sub>	0.0769
Antimony.....	Sb <sub>2</sub> O <sub>3</sub>	Sb	0.7897
	Sb <sub>2</sub> S <sub>3</sub>	Sb	0.7145
Arsenic.....	As <sub>2</sub> S <sub>3</sub>	As	0.6093
	.....	As <sub>2</sub> O <sub>3</sub>	0.8043
	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub>	As	0.4827
	.....	As <sub>2</sub> O <sub>3</sub>	0.6372
	.....	As <sub>2</sub> O <sub>5</sub>	0.7402
Barium.....	BaSO <sub>4</sub>	Ba	0.5885
	.....	BaO	0.6571
Bismuth .....	Bi <sub>2</sub> O <sub>3</sub>	Bi	0.8972
	BiOCl	Bi	0.8021
	.....	Bi <sub>2</sub> O <sub>3</sub>	0.8944
	Bi <sub>2</sub> S <sub>3</sub>	Bi	0.8122
Bromine.....	AgBr	Br	0.4256
	.....	HBr	0.4309
Cadmium.....	CdO	Cd	0.8754
	CdS	....	0.7781
	CdSO <sub>4</sub>	....	0.5391
Calcium.....	CaO	Ca	0.7148
	CaCO <sub>3</sub>	CaO	0.5604
Chlorine.....	AgCl	Cl	0.2472
	.....	HCl	0.2543
Chromium.....	Cr <sub>2</sub> O <sub>3</sub>	Cr	0.6846
	Cr	Cr <sub>2</sub> O <sub>3</sub>	1.4606
	PbCrO <sub>4</sub>	Cr	0.1613
	BaCrO <sub>4</sub>	Cr	0.2055
	Co <sub>3</sub> O <sub>4</sub>	Co	0.7345
Cobalt.....	Cu	CuO	1.2516
Copper.....	CuO	Cu	0.7990
	Cu <sub>2</sub> S	Cu	0.7987
Iodine.....	AgI	I	0.5403
	.....	HI	0.5446
Iron.....	Fe <sub>2</sub> O <sub>3</sub>	Fe	0.6996
	.....	FeO	0.8999
Lead.....	PbO	Pb	0.9282
	PbS	Pb	0.8658
	.....	PbO	0.9328
	PbSO <sub>4</sub>	Pb	0.6829
	.....	PbO	0.7358
	PbCrO <sub>4</sub>	Pb	0.6406
	.....	PbO	0.6901

## CHEMICAL FACTORS—Continued

	Weighed.	Required.	Factor
Magnesium.....	MgO	Mg	0.6036
	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	MgO	0.3624
	MgSO <sub>4</sub>	....	0.3352
Manganese.....	Mn <sub>2</sub> O <sub>4</sub>	Mn	0.7205
	MnSO <sub>4</sub>	....	0.3641
Mercury.....	HgS	Hg	0.8618
	HgO	....	0.9259
Nickel.....	NiO	Ni	0.7857
	Ni	NiO	1.2726
Phosphorus.....	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ..	P	0.2784
	.....	P <sub>2</sub> O <sub>5</sub>	0.6376
	(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> (MoO <sub>3</sub> ) <sub>12</sub>	P <sub>2</sub> O <sub>5</sub>	0.0378
Platinum.....	(NH <sub>4</sub> Cl) <sub>2</sub> PtCl <sub>4</sub>	Pt	0.4417
	K <sub>2</sub> PtCl <sub>6</sub>	Pt	0.4035
Potassium.....	KCl	K <sub>2</sub> O	0.6320
	K <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> O	0.5408
	K <sub>2</sub> PtCl <sub>6</sub>	K <sub>2</sub> O	0.1941
Selenium.....	SeO <sub>2</sub>	Se	0.7826
Silver.....	AgCl	Ag	0.7528
Sodium.....	NaCl	Na <sub>2</sub> O	0.5308
	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> O	0.4368
Sulphur.....	BaSO <sub>4</sub>	S	0.1373
	BaSO <sub>4</sub>	SO <sub>3</sub>	0.3429
Tellurium.....	TeO <sub>2</sub>	Te	0.8020
Tin.....	SnO <sub>2</sub>	Sn	0.7879
Tungsten.....	WO <sub>3</sub>	W	0.7931
Uranium.....	(UO <sub>2</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	U	0.6681
	.....	U <sub>3</sub> O <sub>8</sub>	0.7877
Vanadium.....	Vd <sub>2</sub> O <sub>5</sub>	Vd	0.5614
Zinc.....	ZnO	Zn	0.8035



## STANDARD SOLUTIONS

Ammonia water.....	Take 55.6 cc. ammonia water (sp.gr. 0.9) and dilute to one liter. One cc. will = 0.017 gram $\text{NH}_3$ .
Ammonium molybdate.....	4.25 grams of the crystallized salt to the liter. One cc.=0.005 gram Pb.
Ammonium sulphocyanate .	7.617 grams to the liter. One cc.=0.0025 gram As. =0.0108 gram Ag.
Hydrochloric acid.....	Take 74.5 cc. of hydrochloric acid (sp.gr. 1.2) and add water to make a liter. One cc. will contain 0.0365 gram HCl.
Iodine solution.....	Dissolve 9.7 grams of iodine in small amount of water with 14 grams of potassium iodide and dilute to one liter. One cc.=0.005 gram Sn.
Nitric acid.....	Take 86.2 cc. of nitric acid (sp.gr. 1.42) and add water to make a liter. One cc. will contain 0.063 gram $\text{HNO}_3$ .
Oxalic acid.....	Dissolve 63 grams of the crystals in a liter of water to make a normal solution in which one cc. will equal 0.045 gram $\text{C}_2\text{O}_4\text{H}_2$ . One cc.=0.0275 gram Mn.
Potassium dichromate.....	4.39 grams to the liter. One cc.=0.005 gram Fe.
Potassium bromate.....	2.7852 grams to liter. One cc.=0.005 gram Sb.
Potassium chromate.....	4.9 grams of Merck's to the liter. One cc.=0.005 gram Pb.
Potassium ferrocyanide ....	22 grams to the liter. One cc.=0.005 grams Zn. =0.0043 gram Cd. =0.011 gram Pb.
Potassium hydroxide.....	56 grams of purest KOH to the liter. One cc. contains 0.056 gram KHO.
Potassium iodide.....	8.3 grams to the liter. One cc.=0.005 gram Hg.
Potassium permanganate...	2.83 grams to the liter. One cc.=0.005 gram Fe. =0.0025 gram $\text{CaO}$ . =0.0094 gram Pb. =0.00286 gram Mo. =0.001476 gram Mn. =0.005375 gram Sb.
Sodium hydroxide.....	40 grams to the liter. One cc.=0.04 NaOH.

Sodium thiosulphate . . . . .	19 grams to liter. One cc. = 0.005 Cu.
Silver nitrate . . . . .	16.997 grams to the liter.
	One cc. = 0.003545 gram Cl
	= 0.003645 gram HCl.
	= 0.002596 gram CN.
Uranium acetate . . . . .	4 grams dissolved in 25 cc. acetic acid and diluted to liter.
	One cc. = 0.005 gram As.
	= 0.00473 gram $P_2O_5$ .

## INDICATOR SOLUTIONS

Ammonio-ferric alum . . . . .	Dissolve one gram in 100 cc. of distilled water.
Cochineal . . . . .	Dissolve three grams in 100 cc. of alcohol and dilute with water to 500 cc.
Indigo . . . . .	Add slowly one gram to five cc. of fuming sulphuric acid with constant stirring and dilute as desired with water.
Litmus . . . . .	Dissolve one gram in 50 cc. of water.
Methyl orange . . . . .	Dissolve one gram in a liter of water.
Phenolphthalein . . . . .	Dissolve one gram in 35 cc. of dilute alcohol.
Potassium ferricyanide . . . . .	Dissolve as needed in the proportion of one gram to 100 cc. of water.
Silver nitrate . . . . .	Dissolve one-tenth of a gram in 100 cc. of water.
Starch solution . . . . .	Boil one gram of starch with half a liter of water.
Tannic acid . . . . .	Dissolve one gram in 200 cc. of water.

## COMMON ORE MINERALS

Name.	Composition.	Metal.	Specific Gravity
		Per Cent.	
Anglesite . . .	Sulphate of lead . . . . .	68.3 lead . . . . .	6.3
Argentite . . .	Sulphide of silver . . . . .	87.1 silver . . . . .	7.3
Arsenopyrite . .	Sulpharsenide of iron . . . . .	46.0 arsenic . . . . .	6.1
Azurite . . . .	Carbonate of copper . . . . .	55.2 copper . . . . .	3.8
Bauxite . . . .	Hydrate of alumina . . . . .	73.9 alumina . . . . .	2.5
Bismuthinite . .	Sulphide of bismuth . . . . .	81.2 bismuth . . . . .	6.4
Bornite . . . .	Sulphide of copper and iron . . . . .	55.5 copper . . . . .	5.2
Braunite . . . .	Silicate of manganese . . . . .	63.0 manganese . . . . .	4.8
Bromyrite . . .	Bromide of silver . . . . .	57.4 silver . . . . .	5.9
Calamine . . . .	Silicate of zinc . . . . .	54.1 zinc . . . . .	3.4
Calaverite . . .	Telluride of gold . . . . .	39.5 gold . . . . .	9.4
Cassiterite . . .	Oxide of tin . . . . .	78.6 tin . . . . .	7.0
Cerargyrite . . .	Chloride of silver . . . . .	75.3 silver . . . . .	5.4
Cerussite . . . .	Carbonate of lead . . . . .	77.5 lead . . . . .	6.5
Chalcocite . . .	Sulphide of copper . . . . .	79.8 copper . . . . .	5.7
Chalcopyrite . .	Sulphide of copper, iron . . . . .	34.5 copper . . . . .	4.2
Chromite . . . .	Oxide of chromium, iron . . . . .	46.5 chromium . . . . .	4.5
Chrysocolla . . .	Silicate of copper . . . . .	36.2 copper . . . . .	2.2
Cinnabar . . . .	Sulphide of mercury . . . . .	86.2 mercury . . . . .	8.1
Cobaltite . . . .	Sulpharsenide of cobalt . . . . .	35.5 cobalt . . . . .	6.2
Covellite . . . .	Sulphide of copper, etc. . . . .	66.4 copper . . . . .	4.6
Cryolite . . . .	Fluoride of aluminum, sodium . . . . .	12.8 aluminum . . . . .	3.0
Cuprite . . . . .	Oxide of copper . . . . .	70.9 copper . . . . .	6.1
Diopase . . . . .	Silicate of copper . . . . .	40.3 copper . . . . .	3.3
Galena . . . . .	Sulphide of lead . . . . .	86.6 lead . . . . .	7.5
Hematite . . . .	Oxide of iron . . . . .	70.0 iron . . . . .	5.0
Hessite . . . . .	Telluride of silver . . . . .	63.3 silver . . . . .	8.7
Hydrozincite . .	Carbonate of zinc . . . . .	60.4 zinc . . . . .	3.7
Limonite . . . .	Oxide of iron . . . . .	59.8 iron . . . . .	3.8
Linarite . . . .	Sulphate of lead, copper, etc. . . . .	51.7 lead . . . . .	5.4
Magnetite . . . .	Oxide of iron . . . . .	72.4 iron . . . . .	5.1
Malachite . . . .	Carbonate of copper . . . . .	57.3 copper . . . . .	3.9
Mimetite . . . .	Arseniate of lead . . . . .	67.5 lead . . . . .	7.1
Minium . . . . .	Oxide of lead . . . . .	90.6 lead . . . . .	4.6
Molybdenite . .	Sulphide of molybdenum . . . . .	60.0 molybdenum . . . . .	4.7
Naumannite . . .	Selenide of silver . . . . .	73.2 silver . . . . .	8.1
Niccolite . . . .	Arsenide of nickel . . . . .	43.9 nickel . . . . .	7.5
Petzite . . . . .	Telluride of silver, gold . . . . .	41.8 silver . . . . .	8.9
Proustite . . . .	Sulpharsenide of silver . . . . .	65.4 silver . . . . .	6.3
Psilomelane . . .	Oxide of manganese . . . . .	58.6 manganese . . . . .	4.0
Pyrargyrite . . .	Sulphantimonide of silver . . . . .	59.9 silver . . . . .	5.8
Pyrite . . . . .	Sulphide of iron . . . . .	46.6 iron . . . . .	5.0

COMMON ORE MINERALS—*Continued*

Name.	Composition.	Metal.	Specific Gravity
		Per Cent.	
Pyrolusite ...	Oxide of manganese.....	50.0 manganese ..	4.8
Pyromorphite	Phosphochloride of lead .....	76.3 lead . . . . .	6.9
Pyrrhotite...	Sulphide of iron.....	46.6 iron.....	5.0
Siderite .....	Carbonate of iron.....	48.2 iron.....	3.8
Smithsonite .	Carbonate of zinc.....	52.1 zinc.....	4.4
Sphalerite ...	Sulphide of zinc.....	67.0 zinc.....	4.1
Sperryllite ...	Arsenide of platinum .....	56.5 platinum....	10.6
Stannite.....	Sulphide of tin, etc. ....	27.5 tin.....	5.2
Stephanite . .	Sulphantimonide of silver ...	68.5 silver .....	6.2
Stibnite .....	Sulphide of antimony.....	71.4 antimony ...	4.6
Stolzite .....	Tungstate of lead.....	49.0 lead.....	7.9
Stromeyerite	Sulphide of silver, copper ...	53.1 silver.....	6.2
Sylvanite.....	Telluride of gold .....	24.5 gold.....	8.1
Tenorite.....	Oxide of copper.....	79.8 copper.....	5.9
Tetrahedrite .	Sulphide of copper, etc.....	57.5 copper.....	4.9
Willemitite ...	Silicate of zinc.....	58.6 zinc.....	4.1
Wulfenite'...	Molybdate of lead.....	56.3 lead.....	6.9
Wurtzite ....	Sulphide of zinc.....	67.0 zinc.....	4.0
Zincite.....	Oxide of zinc.....	80.3 zinc.....	5.6

## TABLE OF WEIGHTS AND MEASURES

## WEIGHTS

1 grain troy = 0.0648004 gram.  
 1 pound troy = 0.822857 pound avoirdupois.  
 1 pound avoirdupois = 7000 grains troy = 1.215279 pounds troy.

## TROY WEIGHT

1 pound = 12 oz. = 240 dwts. = 5760 grains = 373.2418 grams.  
 1 oz. = 20 dwts. = 480 grains = 31.1035 grams.  
 1 dwt. = 24 grains = 1.5552 grams.  
 1 grain = 0.0648 gram.  
 1 gram = 15.432 troy grains.

## AVOIRDUPOIS WEIGHT

1 ton = 20 hundredweight = 2240 pounds = 1016.04 kilograms.  
 1 hundredweight = 112 pounds = 50.80 kilograms.  
 1 pound = 16 ounces = 256 drams = 7000.00 grains = 453.5900 grams.  
 1 ounce = 16 drams = 437.50 grains = 28.3495 grams.  
 1 dram = 27.34 grains = 1.7718 grams.  
 1 net ton = 2000 pounds = 2916.666 ozs. troy = 907.19 kilograms.

## METRIC TON

1 metric ton = 1000 kilograms.

## MEASURE OF CAPACITY

*A. Dry Measure*

1 bushel = 2150.42 cubic inches.  
 1 bushel = the volume of 77.627 pounds of distilled water at 40° C.  
 Legal: 1 liter = 0.908 quart.  
 1 bushel = 4 pecks = 8 gallons = 32 quarts = 35.24229 liters.  
 1 peck = 2 gallons = 8 quarts = 8.81057 liters.  
 1 gallon = 4 quarts = 4.40528 liters.  
 1 quart = 1.10132 liters.

*B. Liquid Measure*

1 U. S. gallon = 231 cubic inches.  
 1 gallon = the volume of 8.3388822 pounds = 58378 troy grains of distilled water at 40° C. (Stillman, "Engineering Chemistry.")  
 1 gallon = 58318 grains of water at 62° F. (U. S. Phar.)

1 gallon = 58334.9 + grains of pure water at 60° F., weighed in air at 60° F. at barometric pressure of 30 inches of mercury.  
(Mason, "Examination of Water.")

Legal: 1 liter = 1.0567 quart = 0.26417 gallon.

1 gallon = 4 quarts = 8 pints = 32 gills = 3.78544 liters.

1 quart = 2 pints = 8 gills = 0.94636 liter.

1 pint = 4 gills = 0.47318 liter.

1 gill = 0.118295 liter.

1 cubic foot = 7.48 gallons = 28.315 liters = 62.42 pounds of water at 60° F. (Stillman.)

1 cubic foot of water at 62° F. = 62.355 pounds avoirdupois = 28320 grams.

1 cubic inch of water at 62° F. = 0.0361 pounds avoirdupois = 16.387 grams. (Watts' "Dictionary," V., 1010.)

#### LINEAR MEASURE

1 yard = 0.91440 meter.

1 foot = 0.30480 meter.

1 inch = 0.0254 meter.

39.37 inches = 1 meter.

#### CONVERSION OF THERMOMETER READINGS

To convert Fahrenheit to Centigrade, subtract 32 and multiply by  $\frac{5}{9}$ .

To convert Centigrade to Fahrenheit, multiply by  $\frac{9}{5}$  and add 32.

#### TABLE OF MEXICAN WEIGHTS

600 grains = 1 ounce.

8 ounces = 1 marc.

16 ounces = 1 pound.

25 pounds = 1 arroba.

100 pounds = 1 quintal.

300 pounds = 1 carga.

3200 pounds = 1 monton.

In some localities 350 pounds equal 1 carga.

EQUIVALENTS OF OUNCES TROY PER TON OF 2000 LBS.  
IN GRAMS PER METRIC TON

Ozs.	Grms.	Ozs.	Grms.	Ozs.	Grms.	Ozs.	Grms.
0.01	0.34	0.31	10.62	0.61	20.91	0.91	31.20
0.02	0.68	0.32	10.97	0.62	21.25	0.92	31.54
0.03	1.02	0.33	11.31	0.63	21.60	0.93	31.88
0.04	1.37	0.34	11.65	0.64	21.94	0.94	32.22
0.05	1.71	0.35	12.00	0.65	22.28	0.95	32.57
0.06	2.05	0.36	12.34	0.66	22.62	0.96	32.91
0.07	2.40	0.37	12.68	0.67	22.97	0.97	33.25
0.08	2.74	0.38	13.02	0.68	23.31	0.98	33.60
0.09	3.08	0.39	13.37	0.69	23.65	0.99	33.94
0.10	3.42	0.40	13.71	0.70	24.00	1.00	34.28
0.11	3.77	0.41	14.05	0.71	24.34	2.00	68.57
0.12	4.11	0.42	14.40	0.72	24.68	3.00	102.85
0.13	4.45	0.43	14.74	0.73	25.02	4.00	137.14
0.14	4.80	0.44	15.08	0.74	25.37	5.00	171.43
0.15	5.14	0.45	15.42	0.75	25.71	6.00	205.71
0.16	5.48	0.46	15.77	0.76	26.05	7.00	240.00
0.17	5.82	0.47	16.11	0.77	26.40	8.00	274.28
0.18	6.17	0.48	16.45	0.78	26.74	9.00	308.57
0.19	6.51	0.49	16.80	0.79	27.08	10.00	342.86
0.20	6.85	0.50	17.14	0.80	27.42	15.00	514.29
0.21	7.20	0.51	17.48	0.81	27.77	20.00	685.72
0.22	7.54	0.52	17.82	0.82	28.11	25.00	857.15
0.23	7.88	0.53	18.17	0.83	28.45	30.00	1028.58
0.24	8.22	0.54	18.51	0.84	28.80	40.00	1371.44
0.25	8.57	0.55	18.85	0.85	29.14	50.00	1714.30
0.26	8.91	0.56	19.20	0.86	29.48	60.00	2057.16
0.27	9.25	0.57	19.54	0.87	29.82	70.00	2400.02
0.28	9.60	0.58	19.88	0.88	30.17	80.00	2742.88
0.29	9.94	0.59	20.22	0.89	30.51	90.00	3085.74
0.30	10.28	0.60	20.57	0.90	30.85	100.00	3428.60

EQUIVALENTS OF GRAMS PER METRIC TON IN OUNCES  
TROY PER TON OF 2000 POUNDS

Grams.	Troy Ozs.	Grams.	Troy Ozs.
0.1	0.0029	10	0.2916
0.2	0.0058	20	0.5833
0.3	0.0087	30	0.8749
0.4	0.0116	40	1.1666
0.5	0.0145	50	1.4583
0.6	0.0175	60	1.7499
0.7	0.0203	70	2.0316
0.8	0.0233	80	2.3332
0.9	0.0262	90	2.6249
1.0	0.0292	100	2.9166
2.0	0.0583	200	5.8332
3.0	0.0875	300	8.7498
4.0	0.1166	400	11.6664
5.0	0.1458	500	14.5830
6.0	0.1749	600	17.4996
7.0	0.2042	700	20.4162
8.0	0.2332	800	23.3328
9.0	0.2625	900	26.2494
		1000	29.1660



## EQUIVALENTS OF AVOIRDUPOIS POUNDS IN KILOGRAMS

Pounds.	Kilograms.	Pounds.	Kilograms.
0.1	0.0453	100	45.356
0.2	0.0907	200	90.718
0.3	0.1361	300	136.078
0.4	0.1814	400	181.436
0.5	0.2268	500	226.780
0.6	0.2722	600	272.155
0.7	0.3175	700	317.514
0.8	0.3629	800	362.874
0.9	0.4082	900	408.233
1.0	0.4535	1,000	453.559
2.0	0.9072	2,000	907.183
3.0	1.3607	3,000	1360.777
4.0	1.8143	4,000	1814.366
5.0	2.2678	5,000	2267.796
6.0	2.7215	6,000	2721.554
7.0	3.1751	7,000	3175.147
8.0	3.6287	8,000	3628.739
9.0	4.0823	9,000	4082.332
10.0	4.5356	10,000	4535.592
20.0	9.0718	20,000	9071.829
30.0	13.6078	30,000	13607.773
40.0	18.1436	40,000	18143.659
50.0	22.6779	50,000	22677.962
60.0	27.2155	60,000	27215.545
70.0	31.7515	70,000	31751.469
80.0	36.2874	80,000	36287.394
90.0	40.8233	90,000	40823.318
		100,000	45355.924

## EQUIVALENTS OF KILOGRAMS IN AVOIRDUPOIS POUNDS

Kilos.	Pounds.	Kilos.	Pounds.
0.1	0.2204	100	220.462
0.2	0.4409	200	440.924
0.3	0.6613	300	661.386
0.4	0.8818	400	881.848
0.5	1.1023	500	1102.310
0.6	1.3227	600	1322.772
0.7	1.5432	700	1543.234
0.8	1.7636	800	1763.696
0.9	1.9841	900	1984.158
1.0	2.2046	1,000	2204.62
2.0	4.4092	2,000	4409.24
3.0	6.6138	3,000	6613.86
4.0	8.8184	4,000	8818.48
5.0	11.0231	5,000	11023.10
6.0	13.2277	6,000	13277.72
7.0	15.4323	7,000	15432.34
8.0	17.6369	8,000	17636.96
9.0	19.8415	9,000	19841.58
10.0	22.0462	10,000	22046.2
20.0	44.0924	20,000	44092.4
30.0	66.1386	30,000	66138.6
40.0	88.1848	40,000	88184.8
50.0	110.2310	50,000	110231.0
60.0	132.2727	60,000	132277.2
70.0	154.3234	70,000	154323.4
80.0	176.3696	80,000	176369.6
90.0	198.4158	90,000	198415.8
100.0	220.462	100,000	220462.0

## EQUIVALENTS OF AVOIRDUPOIS POUNDS IN KILOGRAMS

Pounds.	Kilograms.	Pounds.	Kilograms.
0.1	0.0453	100	45.356
0.2	0.0907	200	90.718
0.3	0.1361	300	136.078
0.4	0.1814	400	181.436
0.5	0.2268	500	226.780
0.6	0.2722	600	272.155
0.7	0.3175	700	317.514
0.8	0.3629	800	362.874
0.9	0.4082	900	408.233
1.0	0.4535	1,000	453.559
2.0	0.9072	2,000	907.183
3.0	1.3607	3,000	1360.777
4.0	1.8143	4,000	1814.366
5.0	2.2678	5,000	2267.796
6.0	2.7215	6,000	2721.554
7.0	3.1751	7,000	3175.147
8.0	3.6287	8,000	3628.739
9.0	4.0823	9,000	4082.332
10.0	4.5356	10,000	4535.592
20.0	9.0718	20,000	9071.829
30.0	13.6078	30,000	13607.773
40.0	18.1436	40,000	18143.659
50.0	22.6779	50,000	22677.962
60.0	27.2155	60,000	27215.545
70.0	31.7515	70,000	31751.469
80.0	36.2874	80,000	36287.394
90.0	40.8233	90,000	40823.318
		100,000	45355.924

EQUIVALENTS OF KILOGRAMS IN AVOIRDUPOIS POUNDS

Kilos.	Pounds.	Kilos.	Pounds.
0.1	0.2204	100	220.462
0.2	0.4409	200	440.924
0.3	0.6613	300	661.386
0.4	0.8818	400	881.848
0.5	1.1023	500	1102.310
0.6	1.3227	600	1322.772
0.7	1.5432	700	1543.234
0.8	1.7636	800	1763.696
0.9	1.9841	900	1984.158
1.0	2.2046	1,000	2204.62
2.0	4.4092	2,000	4409.24
3.0	6.6138	3,000	6613.86
4.0	8.8184	4,000	8818.48
5.0	11.0231	5,000	11023.10
6.0	13.2277	6,000	13277.72
7.0	15.4323	7,000	15432.34
8.0	17.6369	8,000	17636.96
9.0	19.8415	9,000	19841.58
10.0	22.0462	10,000	22046.2
20.0	44.0924	20,000	44092.4
30.0	66.1386	30,000	66138.6
40.0	88.1848	40,000	88184.8
50.0	110.2310	50,000	110231.0
60.0	132.2727	60,000	132277.2
70.0	154.3234	70,000	154323.4
80.0	176.3696	80,000	176369.6
90.0	198.4158	90,000	198415.8
100.0	220.462	100,000	220462.0

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1. The first group of people who are interested in the results of the study are the researchers themselves. They want to know if the study was successful in achieving its goals and if the data collected is reliable and valid.

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